

Mary L. Hossler

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A LABORATORY OUTLINE
OF
ORGANIC CHEMISTRY

BY
LAUDER WILLIAM JONES
PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF CINCINNATI



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PREFACE.

TEXT-BOOKS which treat of the experimental aspect of organic chemistry are already so abundant that the issuing of a new book of this kind would seem to demand some very convincing apology on the part of the author.

The major part of the material included in this book has formed the subject matter of a number of distinct courses which I conducted in the University of Chicago during the years 1897-1907. These courses were planned for large classes, and were arranged to meet the needs of students with diversified interests in chemistry. The classes included students in the College of Liberal Arts and in the School of Science; premedical students and medical students; students somewhat more advanced who came for summer courses; and graduate students. Since 1907 the same outlines have been in use at the University of Cincinnati, and have been made to include certain phases of the subject particularly suited to students of chemical engineering.

Mimeographed sheets were employed, and were revised each year so as to include precautions and changes which actual experience in teaching suggested as desirable to make the directions as free as possible from the ambiguity so difficult to avoid in description of this kind.

From this brief history it will be apparent that the present selection of problems has been determined by the need of meeting educational demands both varied and complicated.

Within the past few years the science of chemistry has pressed over its boundaries far into neutral territory, where with other sciences, — once almost alien, — it has met for the purpose of forming a closer alliance which augurs great mutual benefit to all. As a result of this increased coöperation, it has come about that students engaged in the study of those sciences which border closely upon chemistry, can no longer rest content to follow the old-time practice of acquiring a knowledge of chemistry through

a brief, and frequently unprofitable period of dabbling in an elementary laboratory; or through listening impatiently to a few meager lectures designed for a special clan of workers, and arranged with the avowed purpose of giving the least possible amount of chemistry with the least expenditure of time.

In most institutions of learning there has grown up an increasing demand for more intensive as well as extensive training in elementary chemistry; and this has brought about corresponding changes in the curriculum of chemistry. Experimental organic chemistry, once a mature part of the course, usually preceded by qualitative and quantitative analysis, and requiring a reading knowledge of German and French, now finds itself stranded with general inorganic chemistry as its sole prerequisite.

The majority of laboratory outlines of organic chemistry, although for the most part excellent, are designed primarily for the mature student in chemistry who is able to read and to digest the original articles cited for reference; and for those who are concerned more especially with varied manipulation and method rather than with a systematic survey of the salient facts and relations underlying the science. On the other hand, the few briefer and simpler outlines extant can hardly be regarded as adequate to give the kind of preparatory training which is now being sought in many quarters.

It would seem, therefore, that there is a place for a text-book which shall approach the subject matter of organic chemistry in much the same thorough but elementary fashion that we are wont to employ in laboratory manuals of inorganic chemistry. In other words, there is need of a course in GENERAL ORGANIC CHEMISTRY. It is hoped that this book may occupy a position and supply a demand of this character.

From what has been said already concerning the origin of this outline, it will be self-evident that it is not intended that any one student shall perform all the experiments given on the following pages. On the contrary, it has been my practice to choose certain limited sets of experiments to meet the needs of particular classes; and, in some cases, to assign different lists of experiments to different students of the same class. The requirements of each case must decide what choice shall be made.

The experiments have been arranged to follow approximately the usual order of subject matter given in most text-books, and

in most courses of lectures. However, the sections and chapters have been grouped and numbered in such a way that by properly chosen assignments other arrangements are easily possible. Thus, the aliphatic and aromatic compounds of the same class — e.g., hydrocarbons, halogen derivatives, alcohols and phenols — might be considered side by side. Similar processes, such as oxidation, reduction, esterification, condensation, might be grouped together for comparative study. Other similar selections will suggest themselves. Many of the experiments have been used for lecture demonstration.

The questions which are appended to each section are by no means intended to exhaust the possibilities in that direction. They are merely a few questions which I have found to be valuable in arousing students to assume an inquiring attitude towards the work. Explanations of the processes, descriptive matter to elucidate reactions, and equations have been omitted advisedly. It is to be presumed that upon a shelf in the laboratory there will be a number of the best reference works on organic chemistry to which the student may be sent for such descriptive matter.

In conclusion, I wish to acknowledge my indebtedness to the many excellent texts on organic chemistry by Emil Fischer, Ludwig Gattermann, F. W. Henle, W. A. Noyes, Julius Cohen, and others. Very many suggestions have been taken from the comprehensive work by S. P. Mulliken entitled "The Identification of Pure Organic Compounds." I wish to express my obligations to Dr. Martin Fischer, head of the Department of Physiology in the University of Cincinnati, for the chapter on colloids. The drawings for the illustrations were made by Mr. Howard A. Dorsey, whom I wish to thank for the personal interest which he took in making them. There must be other debts which I owe and would gladly proclaim at this time; but, at the close of the slow process of accretion by which a collection of this kind is shaped to appear in published form, the various elements become so interwoven that the actual sources of many details cease to be clearly defined in the thought of the author.

LAUDER WILLIAM JONES.

UNIVERSITY OF CINCINNATI,
February 21, 1911.

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DIRECTIONS FOR THE LABORATORY

General Directions.

I. Provide yourself with a note-book. A record of each experiment and answers to all the questions should be put in the note-book. In all equations use the *constitutional formulæ*, not the *empirical formulæ*. An equation, however, will not be sufficient; it should be accompanied by a brief account of the process, not a mere copy of the directions, but a statement of the reasons for the various steps in the operation. If desired, a rough sketch of the apparatus may be put in also.

II. In the case of a few long experiments, two students may work together. These experiments are marked "For two Students." In all other preparations, the work must be entirely independent.

III. It is the object of the actual preparation to obtain pure compounds. Whenever it is possible, the degree of purity should always be ascertained by a determination of the melting-point or of the boiling-point of the finished product.

Concerning Apparatus.

IV. When the apparatus has been checked, clean it thoroughly before putting it away in the desk.

V. Prepare a water-bottle for distilled water.

VI. Cut a glass rod into pieces 6 to 8 inches long, and round the rough ends of each piece by heating them in a flame.

VII. See that you have two pieces of rubber tubing long enough to connect the condenser with the water supply.

VIII. At all times, apparatus not actually in use, which tends to accumulate on the top of the desk, should be cleared away; a desk with plenty of working space will enable you to accomplish more work during a laboratory period.

Concerning Weights and "Yields."

IX. For all preparations, the prescribed amounts must be weighed on an ordinary chemical balance. Do not guess at the amounts.

X. When the yield is called for at the close of an experiment, note the amount of *pure* product, and compare this with the

amount theoretically obtainable. By the amount "theoretically obtainable" is meant the weight of the substance which would be obtained if the reaction proceeded completely in one direction according to the equation.

Laboratory Precautions.

XI. Whenever substances are used which have unpleasant odors or evolve injurious gases (e.g., ammonia, bromine, hydrogen sulphide, hydrochloric acid, amyl alcohol, etc.), the operation must be conducted under a hood.

XII. Vessels or apparatus containing volatile materials to be heated, or in which gases or vapors are evolved, must not be closed air-tight.

XIII. Inflammable liquids, such as ether, ligroïne, benzene, etc., in quantities of more than a few cubic centimeters, must not be heated over a free flame, but in vessels immersed in appropriate baths (water, paraffine, etc.). When such liquids are to be removed by distillation, always employ a condenser.

XIV. Do not put combustible substances in the jars provided for solid waste materials.

Abbreviations.

XV. The following abbreviations will be used:—

[R]. = Consult a reference book.

[Instructions]. = Consult an instructor before you proceed with the experiment.

(?) = An answer must be given before you continue the preparation. Record these answers in your note-book.

[H]. = Hood.

[S.R.] = Store Room.

[S.S.] = Side Shelf.

Ber. = *Berichte der deutschen chemischen Gesellschaft*.

Ann. = *Liebig's Annalen*.

Am. Chem. J. = *American Chemical Journal*.

J. Am. Chem. Soc. = *Journal of the American Chemical Society*.

PART I.
ALIPHATIC SERIES.

DIVISION 1. MONATOMIC COMPOUNDS.
DIVISION 2. POLYATOMIC COMPOUNDS.

OUTLINE OF ORGANIC CHEMISTRY

CHAPTER I.

FRACTIONAL DISTILLATION AND THE PREPARATION OF ABSOLUTE ALCOHOL.

1. **Fractional Distillation: Separation of a Mixture of Ethyl Alcohol and Water.** Make a mixture containing 100 c.c. of ethyl alcohol (95 per cent.) and 100 c.c. of distilled water. Is there any change in temperature when these two liquids are mixed? Is the total volume of this mixture exactly 200 c.c.? Measure its

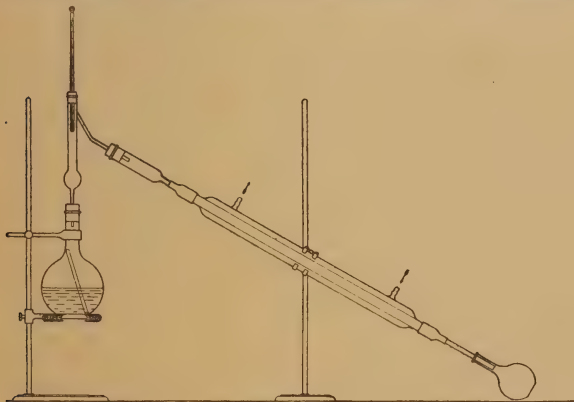


Fig. 1.

volume when it has reached the temperature which the water and alcohol had before mixing. Will the mixture kindle when a flame is applied to it? Pour the dilute alcohol into a 500-c.c. flask fitted with a fractionating-column and a thermometer; and connect the column with a condenser.

Heat a piece of glass tubing in the flame of a Bunsen burner. When the glass is thoroughly softened, remove it from the flame and draw it out slowly, to make a narrow tube 1 mm. in diameter. Cut this narrow tube into pieces about 5 inches long, and seal one end of each piece. Such tubes are called "ebullition tubes." They are used to prevent the violent "bumping" which frequently results because of the superheating of liquids. Put one of these tubes, open end down, into the flask.

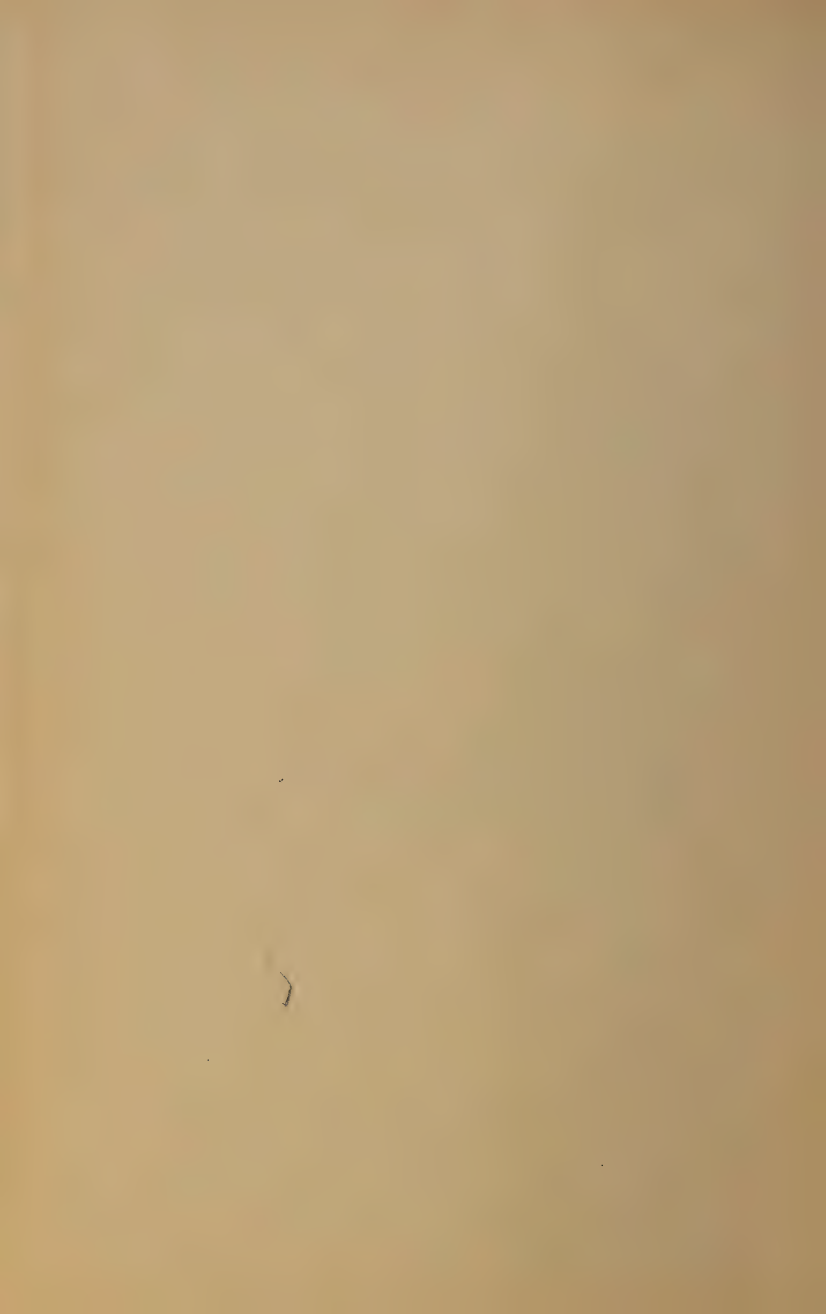
To serve as receivers for the distillate, select four clean, dry flasks (about 100 c.c.), and number them consecutively from 1 to 4. Place the distilling-flask over a wire gauze, and apply heat sufficient to cause the liquid to distill so rapidly that you can still count the drops easily as they fall from the end of the condenser. When the flame has been adjusted, see that it stands exactly under the center of the flask, but do not alter it or remove the burner during the remainder of the distillation.

Collect successively four fractions which boil between the following temperatures:— I, from t_1° – 82° inclusive; II, from 82° – 89° ; III, from 89° – 96° ; IV, from 96° – t_2° . Measure each fraction in a graduated cylinder. In more exact separations, it is frequently desirable to collect fractions at intervals of three to five degrees. This is necessary if the substances have boiling-points very close together. As a rule, substances whose boiling-points lie far apart are much more easily separated. For mixtures which cannot be separated by fractional distillation, consult reference books.

The following scheme will illustrate the method of tabulating your results:—

| Fraction | I | II | III | IV |
|------------------|--------------------------|-------------------------|-------------------------|--------------------------|
| Temperature..... | t_1° – 82° | 82° – 89° | 89° – 96° | 96° – t_2° |
| Volume..... | 67 c.c. | 45 c.c. | 25 c.c. | 57 c.c. |

Second Fractionation. To make a further separation, distill the four fractions one after the other. However, since no one of the fractions has the composition of the original mixtures, the liquids will not pass over completely at the previous tem-



peratures; the alcohol will pass over more rapidly from the solutions stronger in alcohol. As a consequence of this altered distribution, the two end fractions will grow in volume, while the two intermediate fractions will diminish. If this process is repeated several times, the intermediate fractions will soon become practically negligible.

To make the second fractionation, clean the distilling flask and pour the first fraction (t_1° – 82° inclusive) into it. Make the connections previously used, place the flame under the wire gauze, and collect the distillate in flask 1. When the temperature just exceeds 82° , there will still be some liquid left in the distilling-flask. By removing the Bunsen burner, interrupt the boiling at this point, add fraction II (82° – 89°), drop in a new ebullition tube, and resume the distillation without changing the receiving flask. There will be a small amount which will distill before the temperature passes 82° . When the temperature again exceeds 82° , stop the distillation once more, add fraction III (89° – 96°), and proceed as before.

Now add fraction IV (96° – t_2°). Even in this case there may be a slight amount which will boil below 82° . During the treatment of this fraction, when the temperature has reached 82° , do not discontinue the boiling, but change the receiving flask, putting flask 2 in place of flask 1. When the temperature has reached 89° , begin to collect the distillate in flask 3; and at 96° , use flask 4. The following table will show how the results should be recorded.

| Fraction | I | II | III | IV |
|------------------|--------------------------|-------------------------|-------------------------|--------------------------|
| Temperature..... | t_1° – 82° | 82° – 89° | 89° – 96° | 96° – t_2° |
| Volume..... | 94 c.c. | 10 c.c. | 19 c.c. | 70 c.c. |

A third fractionation may be made in stages like those just described for the second. This will lead to a more thorough separation because of the altered composition brought about by the second fractionation. Furthermore, it will be evident that any single fraction, say fraction I (t_1° – 82°), may be subjected to a similar process of fractionation by means of which its separation into alcohol and water could be made more nearly com-

plete.* Try to kindle a sample of fraction I. Does it burn now?

Absolute Ethyl Alcohol.

2. A Test for Water in Alcohol. Put a little pure-white anhydrous copper sulphate in a dry test-tube, and add to it 5 c.c. of ordinary alcohol. Close the test-tube with a tight-fitting stopper, shake it, and allow it to stand for an hour. What change in the appearance of the copper sulphate do you notice? Explain your observation.

The Preparation of Absolute Alcohol. Pour 300 c.c. of ordinary 95 per cent. alcohol into a 1-liter flask. When pieces of good quicklime have been added to the alcohol until they reach the

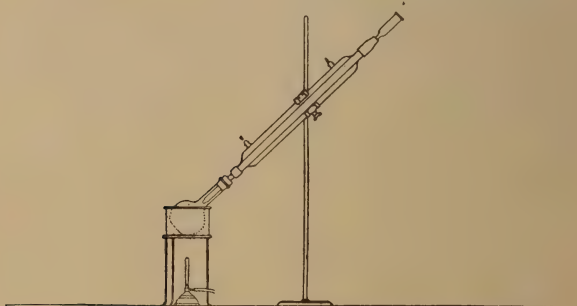


Fig. 2.

surface of it, connect the flask with a reflux-condenser, and heat the flask in a water-bath for an hour. During this time the alcohol should boil gently.

When the water-bath has been removed, and the alcohol has ceased to boil, take the apparatus apart, and adjust the condenser in the usual position for distillation. A clean, dry filter-flask will be found to be the most convenient form of receiver. By means of a sound cork stopper, fasten the filter-flask to the lower end of the condenser, and connect the side tube of the filter-flask with a straight calcium chloride tube, completely

* A mixture of ethyl alcohol and water containing 95.57 per cent. of alcohol has a minimum boiling-point, 78.15° (760 mm.), so that it is not possible by distillation alone to make a separation beyond this point. Pure alcohol boils at 78.3° .

filled with porous calcium chloride. [Instructions]. Do not close this tube with a stopper. Why?

After these connections have been made, place the flask once more in the water-bath, and apply heat enough to cause the alcohol to distill at such a rate that "bumping" is entirely avoided. Collect the first 10 c.c. of the distillate in a small

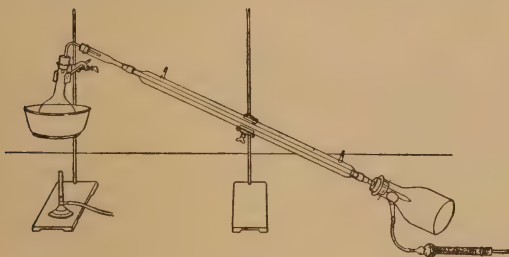


Fig. 3.

flask, and allow the remainder to flow into the filter-flask. Keep the absolute alcohol in a labeled bottle, well corked; it will be needed for later experiments.

a. Is it possible to prepare alcohol absolutely free from water? Apply the test with copper sulphate to the "absolute alcohol" which you have just made.

b. Why do you discard the first portion of the distillate? Do the 10 c.c. which you collected first affect anhydrous copper sulphate?

c. Can you suggest any other reagents which might be employed to remove water from alcohol? What objections would there be to the use of sulphuric acid? of calcium chloride? of phosphorus pentoxide? of phosphorus pentachloride? [R].

CHAPTER II.

THE ALIPHATIC HYDROCARBONS — PARAFFINES, OLEFINES, AND ACETYLENES.

3. Tests for Carbon and Hydrogen in Organic Substances.

In many cases the presence of carbon in a compound may be determined by heating a portion of the substance. If a charring occurs, or if gases are evolved which burn with a smoky flame, carbon is present. Black oxides or finely divided metals, which may be formed by the ignition of certain inorganic salts, must not be mistaken for carbon.

a. Ignite a small quantity of sugar in a porcelain dish. Repeat the experiment, using benzoic acid instead of sugar.

b. Dry 3 or 4 grams of powdered copper oxide by heating it to redness for a few minutes in a small porcelain dish. After sealing one end of a glass tube 4–5 inches long, mix a little benzoic acid with some dry copper oxide; place the mixture at the bottom of the tube, and fill half of the remaining space with dry copper oxide. To permit the carbon dioxide and water vapor to escape freely, hold the tube in a horizontal position, and tap it on the desk so as to form a narrow channel between the oxide layer and the upper wall of the tube. First heat the upper layer of oxide, and then the lower layer containing benzoic acid. Prove that carbon dioxide is evolved. Is there any evidence of the formation of water?

A. *Series of Paraffine Hydrocarbons.*

4. **Methane: Its Preparation from Chloroform.** Put 10 g. of "zinc dust" into a small flask, and cover the powder with dilute alcohol (1 part of water to 5 parts of alcohol). Furnish the flask with a stopper and a delivery-tube, so arranged that any gas evolved may be collected in test-tubes over water. Then add to the flask about 5 c.c. of chloroform and 1 c.c. of copper sulphate solution. The action will commence in the

course of a few seconds, and may become too rapid unless the flask is cooled slightly from time to time.

a. Test the inflammability of the gas. What caused the slight green mantle of the flame? Would pure methane burn with a green flame [R]?

b. Describe two other methods of preparing methane.

c. How could you prepare chloroform from methane? What name is given to this process?

d. Define the term "alkyl," and point out the relation which alkyl groups bear to the formulæ of paraffine hydrocarbons.

e. How does Kekulé's hypothesis of the linking of the carbon atoms explain the fact that dimethyl and ethyl hydride were found to be identical?

B. Series of Olefine Hydrocarbons.

5. Preparation of Ethylene from Ethyl Alcohol. Pour 25 c.c. of absolute ethyl alcohol into a 1-liter flask, and add 75 c.c. of pure concentrated sulphuric acid in small portions, constantly shaking the mixture. Should the mixture become decidedly warm, cool the flask under the water-tap before you add more acid. Why is it dangerous to pour alcohol or water into concentrated sulphuric acid?

Select a stopper which fits the opening of the flask snugly, and bore two holes in it, — one for the thermometer, and one for a doubly bent delivery-tube which leads to the first of a train of two wash-bottles. Fill each wash-bottle about half-full of a concentrated solution of sodium hydroxide. The gas should pass from the first wash-bottle to the bottom of the second, and from the second wash-bottle, by means of a long, bent delivery-tube, to a pail of water, or a pneumatic trough, where it should be collected in bottles over water. See that the bulb of the thermometer dips below the surface of the liquid in the flask.

When you are sure that all connections are tight, heat the flask cautiously over a wire gauze, or a sand-bath, until the temperature reaches 180°. Regulate the flame so that the temperature may be maintained as nearly as possible at this point, and apply the heat so that a constant stream of gas is obtained, without any violent foaming of the reaction mixture. When a sample of gas collected in a test-tube over water,

burns quietly, fill two 8-ounce tincture bottles and one 8-ounce wide-mouthed bottle with the gas. While you take the apparatus apart, notice the odor of the charred product and gases in the generator flask. Does this suggest the necessity for using sodium hydroxide in the wash-bottles?

a. Pour 1 c.c. of bromine water into one of the tincture bottles. Close the bottle with a stopper, and shake it vigorously. Notice the odor of the colorless liquid. Is there any visible evidence of the separation of a new substance? How would bromine act upon a solution of sulphurous acid?

b. Into the second tincture bottle, pour 1 c.c. of a very dilute solution of potassium permanganate (just rose color), and add 1 c.c. of a solution of sodium carbonate. Close the bottle and shake it. What change occurs? (This is known as von Baeyer's reaction for the "double bond.")

c. Place a wide-mouthed bottle of the gas on the table, and kindle the gas. From the mouthpiece of a water-bottle, immediately pour a stream of water into the bottle. This will displace the gas so that a conspicuous flame may be produced. Is the flame distinctly luminous?

d. By means of a rubber tube connected with a gas-cock, fill two tincture bottles with illuminating-gas. To the gas apply the tests described in *a* and *b*. Can you detect any unsaturated substance in the gas? What are the chief "illuminants" in coal-gas?

e. What would be formed by the action of concentrated sulphuric acid upon ethylene? Does this product differ from the chief compound formed by the action of sulphuric acid upon ethyl alcohol at room temperature? How could you convert ethylene into ethyl alcohol?

6. Chemical Behavior of Paraffine and Olefine Hydrocarbons Compared.

a. To 5 c.c. of amylene, gradually add a solution of bromine (5 per cent.) in carbon tetrachloride.

b. Add a few drops of this same bromine solution (5 per cent.) to 10 c.c. of dry petroleum ether (ligroïne) the boiling-point of which lies between 40° and 60°. What is the chief constituent of petroleum ether of this boiling-point? [R]. Divide the mixture into two equal portions, by pouring one half of it into a second dry test-tube. Allow one tube to stand in a dark

place in the cupboard of your desk, and expose the other tube to direct sunlight. After a few minutes, compare the solutions in the tubes. Breathe across the top of the tubes. What causes the cloud of vapor? What differences do you observe in experiments *a* and *b*? Explain them.

c. How would ethane and ethylene behave when treated with bromine? Is this behavior typical of the two classes of hydrocarbons of which ethane and ethylene are representatives? By what differences in graphic formulæ do we picture to ourselves this difference in behavior?

d. By what series of chemical reactions could you convert ethane into ethylene, and the reverse?

e. Upon analysis, a certain hydrocarbon was found to have the following percentage composition:—Carbon = 92.37 per cent.; hydrogen = 7.63 per cent. What is the simplest empirical formula of this hydrocarbon? The vapor-density (air = 1) was found to be 0.9. What would be the molecular weight, and the formula of this hydrocarbon?

f. If it were found by experiment that 13 g. of this hydrocarbon absorbed 160 g. of bromine, how would you arrive at an equation expressing the course of the reaction, and a formula for the addition product?

C. Series of Acetylene Hydrocarbons.

7. Acetylene: Its Preparation from Calcium Carbide. [H].

Fit a clean, dry flask with a stopper having two openings. Through one of these openings introduce a dropping-funnel; through the other, a tube leading into an empty wash-bottle, where it should end just below the stopper. This empty bottle serves to prevent water from running back through the delivery-tube upon the carbide. When 5 g. of calcium carbide have been placed in the flask, permit water to flow, drop by drop, upon the carbide. [CAUTION!] Do not allow a large quantity of water to come suddenly into contact with the carbide. Do not allow the acetylene to escape any more than is necessary, for the gas is not only offensive, but also poisonous. As soon as a sample of the gas, collected in a test-tube, burns quietly when ignited, fill two tincture bottles and one wide-mouthed bottle with it.

a. Burn the gas contained in the wide-mouthed bottle.
b. To the second bottle of the gas, add a little bromine water. When the color of the bromine is entirely discharged, notice the odor of the liquid. Is there any visible evidence of the formation of a new compound? How does the behavior of acetylene toward bromine compare with that of ethylene and of ethane toward the same reagent? [R].

c. **Cuprous Chloride and Cuprous Acetylene.** Dissolve 5 g. of cupric oxide in 20 c.c. of concentrated hydrochloric acid. When the oxide has dissolved, add 5 g. of copper turnings, and boil the acid until the green color of the solution changes to dark-brown. Pour the solution of the copper salt into a beaker containing water. A white precipitate of cuprous chloride will be formed; by decantation, this should be separated from the acid solution, and dissolved in ammonium chloride and ammonia.*

Pass acetylene into 5 c.c. of this solution. What is formed? [R]. Collect this precipitate upon a small filter, wash it, and dry it. When it is dry, heat a *small* piece of it in the flame.

d. Can acetylene be prepared by the direct union of carbon and hydrogen? [R]. How could you obtain acetylene from ethane, and from ethylene?

* If desired, the solution of cuprous chloride may be made as follows:—To 1 g. of copper sulphate, dissolved in a little water, add about 4 c.c. of concentrated ammonium hydroxide solution and 3 g. of hydroxylamine hydrochloride. Dilute the solution with water until its volume is about 50 c.c. It may be kept colorless by placing it in a tightly-corked bottle containing some copper turnings.

CHAPTER III.

HALOGEN COMPOUNDS. — HALOGEN ALKYLs.

8. Tests for the Halogens in Organic Compounds.

a. To a dilute solution of ethylammonium bromide, add a few drops of a solution of silver nitrate. (?)

b. Add a drop or two of ethyl bromide to a solution of silver nitrate. No immediate precipitate is formed. Explain. Allow the mixture to stand, and observe what happens. Add a solution of silver nitrate to a solution of potassium bromide. What difference do you observe in the behavior of ethyl bromide and potassium bromide? Which of the two is more like ethylammonium bromide in behavior? Explain.

c. Dissolve 1 g. of potassium hydroxide in 10 c.c. of alcohol. By means of nitric acid, acidify 1 c.c. of this solution, known as "alcoholic potash," and add a few drops of a solution of silver nitrate to it. Is any precipitate formed? What impurities, capable of giving a precipitate with a nitric acid solution of silver nitrate, are often present in potassium hydroxide?

d. To 1 c.c. of alcoholic potash, add several drops of ethyl bromide, and boil the liquid gently for two minutes. After diluting the liquid with water, *acidify* it with nitric acid, and add 3 or 4 drops of a solution of silver nitrate. Compare the result with that obtained in *b*.

e. Repeat experiment *d*, but use a drop of phenyl bromide (brom benzene) in place of ethyl bromide. If an oil separates when water is added, enough alcohol should be used to dissolve this oil completely. Then add not more than three or four drops of a solution of silver nitrate. Can bromine in phenyl bromide be detected by this process?

f. Seal a piece of copper wire into the end of a short piece of glass rod. Heat the wire in a Bunsen flame until it ceases to color the flame; dip it into an organic substance which contains a halogen, and heat it again. Test chloroform and phenyl bromide in this way.

g. What would be the effect of heating organic compounds containing halogens with a mixture of fuming nitric acid and silver nitrate in closed vessels at high temperature? How would ignition with calcium oxide affect such compounds?

✓ **9. Ethyl Iodide.** Place 2 g. of red phosphorus in a small flask, and pour upon it 10 c.c. of absolute ethyl alcohol. Add 17 g. of powdered iodine, a portion at a time. Shake the flask after the addition of each portion, and cool it carefully before adding the next portion. When the mixture ceases to become warm spontaneously, cork the flask, place it in a beaker of cold water, and let it stand for 24 hours. Then connect the flask with a reflux-condenser, place it in a water-bath, and heat the water in the bath until the iodide begins to boil. (Cf. Fig. 2.) When the iodide has boiled for 15 minutes, change the position of the condenser, and distill the iodide. [R]. At first apply a gentle heat; finally, heat the bath until the water in it boils vigorously.

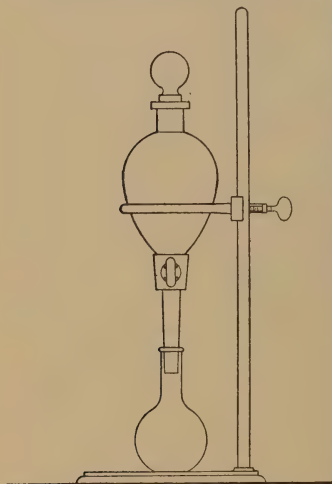


Fig. 4. Separatory-Funnel.

When the liquid ceases to pass into the receiver, transfer the crude product to a small separatory-funnel or a dropping-funnel. [Instructions]. Wash the iodide twice with cold water; then, with a dilute solution of sodium hydroxide until the brown color, caused by iodine, is entirely removed. What impurities are eliminated by these operations? After washing the iodide once more with water, separate it as completely as possible from the water, and place it in a dry flask with solid (not porous) fused calcium chloride which has been broken into pieces about

as large as grains of wheat. It usually requires several hours to dry such preparations completely. Distill it when it is dry. A distilling-flask provided with a thermometer should be used in this distillation. [R]. Observe the boiling-point, and compare

it with the recorded boiling-point of ethyl iodide. Weigh the pure, distilled iodide, and calculate the amount which should

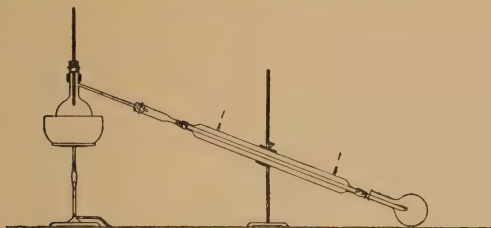


Fig. 5.

have been obtained if all of the alcohol had been changed into iodide according to the equation.

a. Is the iodide heavier, or lighter, than water?

b. When treated with a dilute solution of silver nitrate, does ethyl iodide immediately give a decided precipitate of silver iodide?

c. Can you suggest any other ways of preparing ethyl iodide? How could you make ethyl bromide? propyl chloride?

d. What would be formed if ethyl iodide were treated with zinc dust and dilute alcohol?

✓ **10. Action of Light upon Ethyl Iodide.** Select three small test-tubes of approximately the same size. See that they are dry and clean. Put in each tube about 2 c.c. of the freshly distilled, colorless iodide. Cork the tubes immediately; and place one in direct sunlight, one in diffused light on the desk, and the last one in a dark cupboard or drawer. After 15 minutes, compare the samples of iodide in the three tubes. Return the tubes to their respective places; and, at the end of the laboratory period, compare them again. When the third tube has been kept in the dark for several days, observe whether any change in the color of the iodide has occurred.

Why is it customary to preserve iodides in brown bottles? How do you explain the fact that metallic mercury will discharge the brown color which ethyl iodide acquires on exposure to light?

CHAPTER IV.

MONATOMIC ALCOHOLS AND ETHERS.

11. Reactions of Alcohols.

a. After acidifying 1 or 2 c.c. of a very dilute solution of potassium dichromate with sulphuric acid, add a few drops of alcohol, and boil the solution gently. What changes do you observe? What causes the odor of the mixture? [R]. What class of alcohols will give similar oxidation products? What would be formed by the careful oxidation of isopropyl alcohol?

b. Place 1 or 2 c.c. of ethyl alcohol in a test-tube, and add 0.5 g. sodium [S.R.] cut into small pieces. [CARE!] What gas escapes? When the sodium has disappeared completely, cool the solution. What separates? [R]. Try the same experiment with methyl alcohol in place of ethyl alcohol. Is the reaction which takes place in these two cases a characteristic reaction of alcohols? (Cf. glycol, glycerol.)

c. Mix a few crystals of sodium acetate with a little concentrated sulphuric acid; add a small quantity of ethyl alcohol to the mixture, and heat it gently. Pour the product upon a watch-glass containing 4 or 5 c.c. of water. Notice the odor of the liquid. What is formed? [R]. Try the same test, using amyl or butyl alcohol in place of ethyl alcohol.

d. [H]. To one drop of benzoyl chloride, add three drops of a solution of sodium hydroxide and a few drops of ethyl alcohol; warm the solution, and observe the odor of the mixture. In a similar manner, treat methyl alcohol with benzoyl chloride. This method of making esters is known as Schotten-Baumann's reaction. What is the meaning of the term ester? In what sense are the compounds formed in *c* and in *d* to be classed as esters? Would you call ethyl iodide an ester? Why do we prefer to call compounds of this class esters instead of salts, or ethereal salts?

12. The Methyl Ester of 3,5-Dinitrobenzoic Acid. The odor of a compound, even if it be fairly characteristic, can rarely be depended upon to identify a compound with a high

degree of certainty. As a rule, liquids are not easily purified and separated when very small quantities are available. Chemists, therefore, usually prefer to prepare for identification some crystalline derivative of the compound under inspection. A solid can generally be purified by recrystallization, and, when pure, will have a characteristic melting-point.

Heat 0.3 g. of 3,5-dinitrobenzoic acid and 0.4 g. of phosphorus pentachloride in a very small, dry test-tube, constantly moved above a low flame. Finally, boil the mixture gently for a minute. Pour the product at once upon a small, dry watch-glass. When the acid chloride [R] has solidified, remove the phosphorus oxychloride by pressing the crystals upon a piece of porous plate.

Place the dry substance in a small test-tube, add eight or ten drops of methyl alcohol, and close the tube with a stopper. The reaction will be complete in a few minutes.

To recrystallize the ester, place it in a small flask (60 c.c.), and pour over it about 20 c.c. of dilute ethyl alcohol (3 volumes of alcohol and 1 volume of water). Close the flask with a cork stopper through which an open glass tube, about a foot and a half long, has been inserted. This tube serves as an air condenser to prevent appreciable loss of solvent. Immerse the flask in a water-bath and heat it until the alcohol boils. If the ester does not dissolve completely in the course of a minute or two, add a little more dilute alcohol, and heat the flask again. When sufficient alcohol has been used to dissolve all of the solid, — except, perhaps, a small amount of foreign material, — filter the hot solution rapidly through a small filter-paper to remove insoluble impurities, and cool the filtrate until the ester has separated. Collect the crystals upon a Büchner funnel, and wash them with 4–5 c.c. of cold, concentrated alcohol. When the substance is dry, the melting-point should be determined. The pure substance melts at 107°.

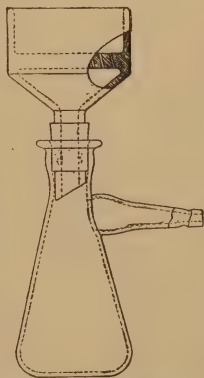


Fig. 6. Büchner Funnel and Filter-Flask.

Other esters of this acid may be employed to identify the corresponding alcohols. They may be prepared according to

the directions just given for the methyl ester. They have the following melting-points (uncorrected):— Ethyl ester, 92° – 93° ; normal propyl ester, 73° – 75° ; normal butyl ester, 64° ; isobutyl ester, 83° – 84° . Cf. Appendix A, Table II.

13. Determination of the Melting-Point. Fill a small beaker two-thirds full of glycerol, or concentrated sulphuric acid, and place it upon a wire gauze on a ring-stand. Pass a thermometer through a small cork, and clamp it by means of this cork so that the bulb of the thermometer is immersed about midway in the glycerine. Bend a piece of glass rod of small diameter so that it forms a stirring-rod triangular at the base, and with a handle which reaches to the top of the beaker where it is bent at an angle.

Capillary-tubes for determining melting-points may be made best from a test-tube. Heat the test-tube in the blast lamp flame until the glass is quite soft; take it from the flame, and draw it out slowly enough to form a narrow tube about 1 mm. in diameter. Pieces of this capillary-tube about 3 inches long may be closed at one end to make the so-called "melting-point tubes."

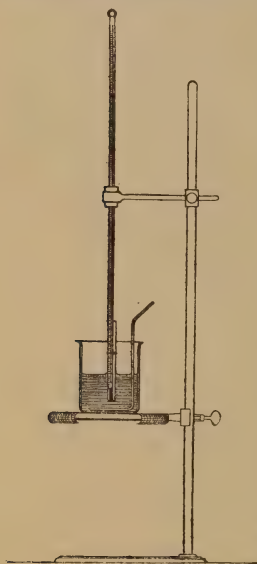


Fig. 7.

A small sample of a dry solid may be put into a tube by taking up a little of the substance with the open end of the tube and tapping the closed end upon the desk. If this small tube, with the sample in it, is then placed against the thermometer in the bath of glycerol, the tube will cling to the side of the thermometer, and should be adjusted so that the sample is opposite the bulb of the thermometer. Some experimenters prefer to fasten the capillary-tubes to the thermometer. This may be done by means of a small rubber ring, made by cut-

ting a narrow cross section from a piece of ordinary gas-hose. Gradually heat the bath of glycerol, and stir it constantly until

the sample of solid softens; at this instant, observe the reading of the thermometer. Concerning corrections, cf. Appendix A, Table II.

Note 1.—For a complete account of the various methods employed in the determination of melting-points, consult Government Bulletin 70, Hygienic Laboratory. A Study of Melting-point Determinations. By George Menge. Washington, 1910.

14. The Iodoform Reaction Applied to Alcohols. Dissolve one drop of the compound to be tested (e.g., ethyl alcohol) in 1 c.c. of water. Place this solution in a small test-tube (3 in.), and, for each cubic centimeter of test liquid, add two drops of a solution of sodium hydroxide (1 : 10). Make a solution of iodine by triturating in a mortar one part of iodine, five parts of potassium iodide, and fifteen parts of water. Drop some of this solution slowly into the cold alkaline solution under inspection, until the liquid has assumed a pale yellow color. When this mixture has stood for two minutes, notice whether any iodoform has separated. At room temperature, isopropyl alcohol and acetone give noticeable precipitates; secondary butyl alcohol forms a precipitate slowly.

If no iodoform separates at room temperature, heat the solution slowly until a thermometer placed in it indicates a temperature of 60°. Maintain this temperature for one minute. If the color of iodine disappears, add more of the iodine solution until the yellow color is permanent. Should no precipitate form, set the tube aside for two minutes. Ethyl alcohol yields an abundant precipitate; while allyl alcohol forms only a slight one; propyl, isobutyl, tertiary butyl, and isoamyl alcohol will not give precipitates within the time prescribed.

15. Tertiary Butyl Alcohol from Acetone. Grignard's Synthesis. Add 4 g. of magnesium turnings to 10 c.c. of dry ether, and pour into the mixture 10 c.c. of methyl iodide. Connect the flask at once with a reflux-condenser, and moderate the action by placing the flask in a bath of cold water. When the metal has nearly disappeared, cautiously add 12 c.c. of dry acetone by pouring it in small portions through the condenser tube.

After the reaction is completed, distill the ether. Acidify the residue with dilute sulphuric acid, and subject the product to distillation. Add solid sodium hydroxide to the distillate, and

separate the upper layer of impure tertiary butyl alcohol. After this has been dried by means of solid sodium hydroxide, distill it. Collect the fraction boiling between 75° and 84° , and freeze it in a mixture of ice and salt. The yield is usually 40–50 per cent.

The boiling-point of pure tertiary butyl alcohol is 82.5° . When pure, it melts at 29° .

16. Diethyl Ether. *Caution! Ether is extremely inflammable. Great care must be taken to keep flames away from any apparatus containing it.* Provide a flask with a stopper which has three openings. Through one of these openings insert a thermometer far enough to reach to the bottom of the flask; through a second opening, pass a tube bent at the proper angle to connect the flask with a condenser; through the third opening, introduce the dropping-tube, long enough to reach nearly

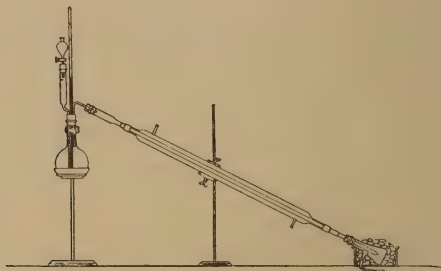


Fig. 8.

to the bottom of the flask. Connect the flask with a condenser which dips into a receiver surrounded by ice-cold water.

Put into the flask a mixture of 75 c.c. of absolute alcohol and 75 c.c. of pure, concentrated sulphuric acid, and heat the flask over a sand-bath until the thermometer indicates a temperature of 140° . During the entire operation, the temperature must be maintained between 140° and 145° .

When the temperature has reached this point, and is practically constant, by means of a cork fasten a dropping-funnel to the upper end of the dropping-tube, and fill the funnel with alcohol; then allow 100 c.c. of alcohol to flow, a drop at a time, to the bottom of the flask. Continue the heating for a few minutes after all of the alcohol has been added. When this

operation is finished, remove the stopper of the flask and notice the odor of the vapors which escape. Explain.

Place the distillate in a separatory-funnel, and wash it several times with small portions of a strong solution of sodium chloride to which a little sodium hydroxide has been added. (?) Finally, shake it several times with small quantities of cold water. What is the specific gravity of ether? [R]. Which layer is ether? The purified ether should be separated, dried over porous calcium chloride for 24 hours, and distilled. What is the boiling-point of pure ether?

a. Shake 2 c.c. of ether with 2 c.c. of water. Add 20 c.c. of water, and shake the mixture again. Result? Place 7 c.c. of water in a small, narrow test-tube, and mark the height of the water by means of a narrow strip of a label. Add 3 c.c. of ether, close the tube, and shake the mixture vigorously. When the ether has separated, paste another narrow strip of label on the tube to mark the line of separation between water and ether. Empty this mixture out, and repeat the experiment, using 7 c.c. of a saturated solution of salt in place of water. Is there any difference in the amount of ether dissolved by water and by salt solution? Explain.

b. What intermediate compounds are formed by the action of sulphuric acid upon alcohol? To what class of compounds do they belong?

c. How do you account for the formation of sulphur dioxide and of carbonaceous products in this experiment? What would be formed in large quantities if the temperature of the experiment were 180° instead of 140° ? *

d. Can you suggest any other methods which might be used to prepare diethyl ether? How could you obtain dimethyl ether? methyl ethyl ether?

e. By means of graphic formulæ, point out the relations which diethyl ether and ethyl alcohol bear to water. How could you change diethyl ether into ethyl alcohol?

f. An analysis was made of a compound composed of carbon, hydrogen, and oxygen. An interpretation of the quantitative results and a molecular weight determination led to the empirical formula $C_4H_{10}O$. When this substance was treated with

* J. U. Nef, J. Am. Chem. Soc. **26**, 1549; **30**, 645.

concentrated hydriodic acid, it gave three compounds: (a) CH_3I ; (b) $\text{C}_3\text{H}_7\text{I}$; (c), H_2O . When these two iodides (a) and (b) were acted on by metallic sodium (Würtz reaction), a hydrocarbon was formed which was found to have specific properties entirely different from those possessed by an isomeric hydrocarbon obtained by the interaction of metallic sodium and ethyl iodide. What is the probable constitutional formula of the first hydrocarbon, and of the original compound of the empirical formula $\text{C}_4\text{H}_{10}\text{O}$?

17. Absolute Ether. After shaking in a separatory-funnel 500 c.c. of ordinary ether and 10–15 c.c. of water, draw off the water, and make the following test with it.

To a portion, add a little iodine dissolved in a solution of potassium iodide. When sodium hydroxide has been added until the brown color of the iodine has just disappeared, warm the solution gently for a minute or two. Notice the odor of the solution and the formation of the slight precipitate. Explain.

After washing the ether six or eight times with small quantities of a solution of sodium chloride, transfer the ether to a bottle, and add porous calcium chloride to it. Allow the ether to remain in contact with the calcium chloride for twenty-four hours. Decant the ether into a clean, dry flask, and add sodium wire made with a sodium press, or thin pieces of sodium.

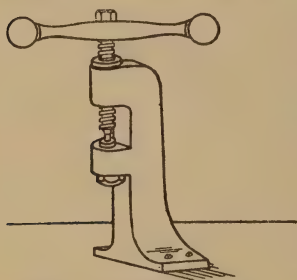


Fig. 9. Sodium Press.

Protect the contents of the flask by an open calcium chloride tube inserted through the stopper. The ether should remain over sodium until the evolution of the gas, which may be quite appreciable at first, has ceased entirely.

CAUTION! Do not pour water into the flask containing the sodium residue. To remove the sodium, add alcohol until the metallic particles have *entirely disappeared*; then add water.

After placing the ether in a clean, dry flask containing 2–3 g. of sodium, it may be distilled and collected in an appropriate receiver. (Cf. § 2, Absolute Alcohol.) The flask containing the ether should be surrounded by water which has been heated to 50° or 60° ; a long condenser should be used.

CHAPTER V.

ALDEHYDES AND KETONES.

Aldehydes.

18. Oxidation of Methyl Alcohol Catalytically Induced by Platinum. Pour 5 c.c. of methyl alcohol into a 250-c.c. Soxhlet flask. Wrap a fine platinum wire around a glass rod of small diameter, so that a spiral about 2 cm. long is formed in the middle section of the wire. Fasten one straight end of this wire around a short piece of glass rod. The length of this straight wire and spiral should be adjusted so that the tip-end of the wire barely touches the surface of the alcohol when it is lowered into the flask and the rod rests upon the top of the

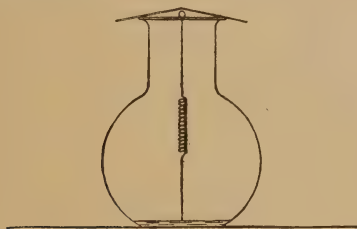


Fig. 10.

flask. Fold a piece of thin asbestos paper so that it forms a trough large enough to cover the mouth of the flask when it is placed loosely upon it.

Heat the platinum wire in a Bunsen flame, lower it quickly into the flask, and cover the flask immediately with the asbestos roof. The odor of the formaldehyde will become apparent at once. If the air supply is properly regulated by adjusting the asbestos cover, the platinum wire will continue to glow for quite a while. After some time, if the liquid in the flask is evaporated, a slight solid residue of paraformaldehyde will remain.

19. Formaldehyde from Methyl Alcohol. A Test for Small Amounts of Methyl Alcohol. Dissolve two drops of methyl

alcohol in 3 c.c. of water contained in a small test-tube. Make a compact spiral of fine copper wire by wrapping it about a glass rod. The spiral should be about 2 cm. long, and should have a straight piece about 20 cm. long. Oxidize the spiral by moving it rapidly through a Bunsen flame, and plunge the red-hot wire into the alcohol solution; repeat this operation several times.

Pour this liquid into a small test-tube, and add one drop of a 0.5 per cent. solution of resorcinol. Cautiously pour this mixture into a second test-tube which contains 4 or 5 c.c. of concentrated sulphuric acid. If the second tube is properly inclined, the mixture will form a distinct layer upon the surface of the acid.

A red zone, slightly violet in color, will appear; and above the zone there will be a light flocculent precipitate. This reaction is characteristic of formaldehyde; other aldehydes do not show this behavior.

20. Formaldehyde. (For two students.) Place 25 c.c. of methyl alcohol in a small distilling-flask, and close the flask with a stopper through which an open glass tube passes to the bottom of the flask. The side tube of the flask should be connected with a piece of hard-glass tubing, in which has been placed a layer of oxidized copper turnings 2 inches long. To oxidize the copper turnings, hold a bundle of them in a pair of crucible tongs, and move them for a few seconds to-and-fro in the flame of a Bunsen burner. (The turnings are usually coated with grease, which should be burned away before they are used.) Close the other end of the hard-glass tube with a stopper and a delivery-tube which leads through a stopper to the bottom of an empty 8-ounce bottle surrounded by a mixture of ice and salt. Through a second opening in the stopper of the bottle, pass a short tube bent at right angle. Be sure that all of the connections are tight. How can you test the apparatus to determine this?

When the tube which leads from the bottle has been attached to the filter-pump by means of a piece of rubber tubing, heat the copper turnings to redness. Place the distilling-flask in a bath of water heated to 65° or 70°, and aspirate a slow stream of air through the entire apparatus, until the alcohol in the distilling-flask has completely volatilized. Be careful not to allow

any condensed alcohol to run down upon the red-hot tube; the tube may break if you do. A loose plug of asbestos placed at

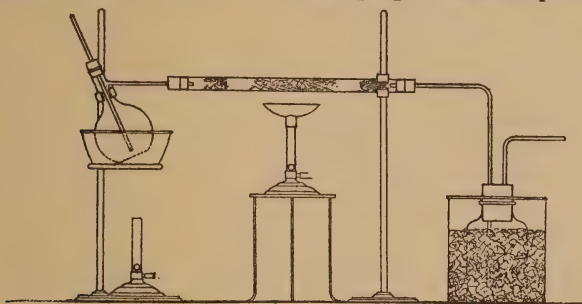


Fig. 11.

each end of the hard-glass tube may prevent this accident. The solution which condenses in the bottle will contain about 40 per cent. formaldehyde; some methyl alcohol and a little formic acid will be present.

a. Filter the liquid. Place most of the solution in an evaporating-dish, and evaporate it over a water-bath. What is left? [R].

b. Add a little of the formaldehyde solution to an ammoniacal solution of silver nitrate, and warm the mixture. To prepare ammoniacal silver nitrate, take a few drops of a solution of silver nitrate, and add ammonium hydroxide to it drop by drop, until the precipitate which forms at first has just dissolved.

c. To a dilute solution of formaldehyde, add a few drops of a 1 per cent. solution of phloroglucinol; then make the solution slightly alkaline by means of sodium hydroxide. No equation need be written.

21. Test for Formaldehyde in Milk. Put 10 c.c. of the milk to be tested into a casserole or small porcelain dish, and add 10 c.c. of concentrated hydrochloric acid which contains 1 drop of a 5 per cent. solution of ferric chloride. Hold the casserole just above a small Bunsen flame, and keep it moving in a rotary fashion until the liquid just reaches the boiling-point. Should formaldehyde be present, a violet color, more or less pronounced, will appear when the temperature reaches 80° or 90°. In the absence of formaldehyde, the liquid will assume a turbid yellowish-brown hue. (Leach's method.)

This test may be carried out somewhat more simply as follows:—Add a few drops of a 5 per cent. solution of ferric chloride to some commercial sulphuric acid. Place the milk to be tested in a large test-tube, and pour into it rapidly 10 c.c. of the prepared acid. If formaldehyde is present, the heat of mixing will be sufficient to develop the violet color. (Hehner's method modified.)

22. Oxidation and Reduction Cell with Formaldehyde and Silver Nitrate.* Apparatus:—Two small beakers of about 60 c.c. capacity; a U tube made by bending the ends of a piece of glass tubing about 4 inches long and 8 mm. in diameter, so that arms 1 inch long are formed; two electrodes made of platinum-foil welded to pieces of platinum wire; a sensitive galvanometer.

Pour some formalin solution into one beaker, and a solution of silver nitrate into the other beaker. Fill the bridge with a dilute solution of potassium nitrate, and close the ends by loose

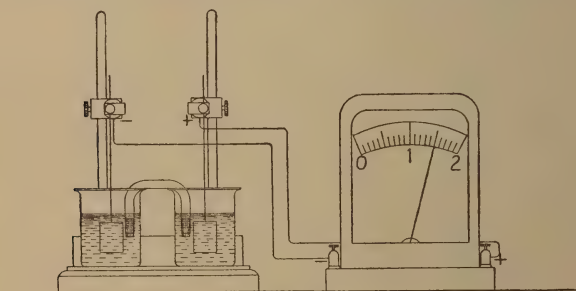


Fig. 12.

rolls of filter-paper. The bridge should be completely filled with this solution. Place the bridge across the beakers, so that the arms dip below the surface of the liquids in the beakers. Immerse a platinum electrode in each beaker, and connect the terminals with the galvanometer. A slight deflection of the needle will be observed.

* For an account of the details of this experiment, and a proposed ionic mechanism whereby alkalies are thought to increase the reducing power of formaldehyde, consult an article by J. Stieglitz, *Science*, Volume 30.

If sodium hydroxide is added to the formalin solution, a very appreciable increase in deflection will be produced, showing that the reducing effect of the formaldehyde is increased by alkalies. On the other hand, the oxidizing effect of the silver nitrate solution may be assumed to depend upon the concentration of silver ions. If this be correct, any reagent which will suppress silver ions should diminish the oxidizing value of this solution. This may be shown by adding ammonium hydroxide — usually employed in the reduction test of aldehyde — to the silver nitrate solution in the beaker; an immediate decrease in the deflection of the needle will be noticed. The formation of complex silver-ammonium ions diminishes the concentration of silver ions.

23. Methylal, Formaldehyde Acetal. Mix 15 g. of para-formaldehyde, 50 g. of methyl alcohol, and 1.5 g. of anhydrous ferric chloride. Place the mixture in a flask attached to a

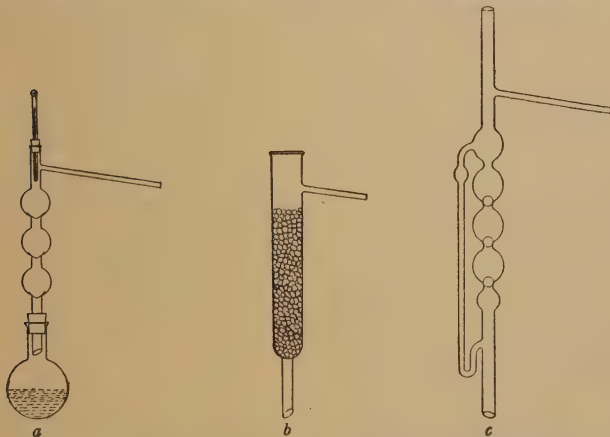


Fig. 13. a. Linnemann's Apparatus; b. Hempel Tube;
c. Glinsky Tube.

reflux-condenser, and heat it for 5–6 hours. Subject the reaction product to distillation, and collect all that passes over below 64°. Redistill the liquid, using a fractionating-column, and collect the low-boiling fraction separately. If this low-boiling portion is placed in a flask connected with a reflux-condenser, and is treated with small pieces of metallic sodium,

it will be freed from methyl alcohol, and will boil, for the most part, between 41° and 43° . The boiling-point of pure methylal is 42° . The yield should be about 90 per cent.

a. Does methylal have the odor of formaldehyde?

b. Would you call methylal an ether; if so, to what alcohols is it related?

c. Does methylal reduce an ammoniacal solution of silver nitrate?

24. Action of Concentrated Sulphuric Acid upon Methylal.

In a small, dry test-tube, treat three drops of methylal with two drops of concentrated sulphuric acid. Heat the acid gradually until it just begins to show signs of boiling. What is the solid white residue deposited upon the cool walls of the tube? Notice the odor of the gas.

25. Acetaldehyde. The Preparation of Aldehyde Ammonia. (For two students.) If this preparation is commenced, it must be carried in one operation as far as the point marked \otimes . It is impossible to interrupt the process at any previous point in the experiment.

Gradually add 75 c.c. of concentrated sulphuric acid to 300 c.c. of water. When the mixture is cold, add to it 125 c.c. of alcohol, and cool the solution thoroughly. Put 100 g. of potassium dichromate, broken into coarse granules, and 50 c.c. of water into a one-liter flask; surround the flask with a freezing-mixture of ice and salt. Pour the mixture of alcohol, acid, and water into a dropping-funnel, and allow it to flow upon the dichromate slowly, and with frequent shaking of the flask. When all the alcohol has been added, allow the flask to remain in the freezing-mixture for 15 minutes.

During this interval, select a sound stopper for the flask. Pass a safety-tube and an adapter through the stopper, connect the adapter with a condenser inclined at an angle of 40° – 50° , and fill the condenser jacket with water which has a temperature of about 30° – 40° . To maintain this temperature during the latter part of distillation, it will be necessary to run a little tap-water into the condenser from time to time. At the upper end of the condenser, insert a long tube which leads to a filter-flask half filled with ether, and surrounded by a freezing-mixture.

Before you remove the flask from the freezing-mixture ask for instructions. When the freezing-mixture is removed, the con-

tents of the flask may soon begin to boil; and unless the boiling is regulated immediately by cooling, the action will quickly become so violent that an explosion may result. It is usually necessary to warm the flask very gently. But as soon as the first signs of boiling are noticed, remove the flame *at once*, and raise the freezing-mixture until it touches the lower part of the flask. In this way, the spontaneous boiling, caused by the heat of chemical action, may be controlled, until the mixture will boil quietly of its own accord. Finally, apply a small flame, which may be raised gradually until a large flame can be used with safety. When the aldehyde has been driven into the ether, disconnect the flask, and notice the odor of the liquid in it. Do you recognize the most pronounced odor? How do you account for its presence?

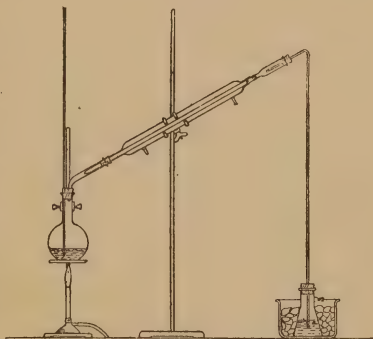


Fig. 14.

If, for lack of time, it is impossible to continue the preparation, the filter-flask which contains the ether solution of aldehyde may be closed air-tight and placed in a cold place until the next laboratory period.

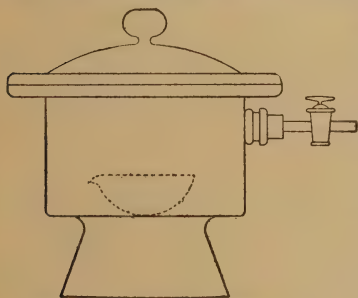


Fig. 15. Vacuum-Desiccator.

⊗. Surround the filter-flask with ice and salt, and saturate the ether with dry ammonia gas obtained from a cylinder. [Instructions]. To avoid stoppage, pass the ammonia into the ether through a wide glass tube, best a straight calcium chloride tube.

It will take fifteen or twenty minutes for this operation. After the crystals of aldehyde ammonia have been collected on a filter, wash them with ether, and dry them until all of the ether has completely

evaporated. This may be done conveniently in a vacuum-desiccator. While using ether, be careful to turn out all flames on your desk.

26. The Preparation of Pure Acetaldehyde from Acetaldehyde Ammonia. Mix 10 g. of aldehyde ammonia, entirely free from ether, with 15 c.c. of water. Place this solution in a dropping-funnel, and let it flow, drop by drop, into a distilling-flask which contains 20 c.c. of water and 8 c.c. of concentrated sulphuric acid. This mixture should be heated in a bath of boiling water while the solution of aldehyde ammonia is dropped into it. Pass the aldehyde through a condenser. The end of the condenser should reach to the bottom of a small distilling-flask which is completely surrounded by a freezing-mixture. [Instructions]. Use a few pieces of porous calcium chloride to dry the aldehyde; and redistill it without transferring it to another flask. After passing the aldehyde through a clean, dry condenser, collect it in a second distilling-bulb which is surrounded with a freezing-mixture. The boiling-point of acetaldehyde is 21° .

a. Reducing Action of Aldehydes. Clean a test-tube with a boiling solution of sodium hydroxide, and place in it 1–2 c.c. of Tollen's reagent. Then add a drop or two of a very dilute solution of aldehyde. With proper precautions, one part of acetaldehyde may be detected in 250,000 parts of water. Cf. § 22.

Note 2. — **Tollen's reagent** may be prepared as follows: — Make a solution containing 0.3 g. of silver nitrate in 3 g. of water; and a second solution containing 0.3 g. of sodium hydroxide in 3 g. of water. Mix these two solutions, and keep the resulting solution in a dark place. It should not be heated.

b. Add 1 drop of aldehyde to 3 drops of Fehling's solution, and warm the mixture gently. What changes occur? Explain them.

Note 3. — **Fehling's solution** can be made by mixing equal volumes of the following solutions: — A solution of copper sulphate containing 34.64 g. in 500 c.c. of water, and a solution containing 180 g. of Rochelle salt and 70 g. of sodium hydroxide in 500 c.c. of water. These two solutions should be mixed just before the reagent is used.



c. **Polymerization of Aldehydes.** By means of a stirring-rod moistened with concentrated sulphuric acid, add a trace, not a drop, of the acid to a little aldehyde cooled in a freezing-mixture. If the aldehyde is thoroughly cooled and stirred with a clean stirring-rod, it will finally solidify. Is the odor still like that of aldehyde? Explain this change. [R].

d. **"Resin" Formation.** Warm a few drops of acetaldehyde with a concentrated solution of sodium hydroxide. How would dilute alkalis act upon acetaldehyde? upon formaldehyde? What is meant by the aldol condensation?

e. Add 1 or 2 drops of acetaldehyde to 10 c.c. of water. To 1 c.c. of this solution, add 1 c.c. of Schiff's reagent (rosaniline sulphite). Try the action of the same reagent upon a similar solution of formaldehyde.

Note 4. — **Schiff's Reagent** may be made by passing sulphur dioxide into a solution of 2.2 g. of rosaniline dissolved in 10 c.c. of cold water, until the solution is saturated with the gas. Rosaniline hydrochloride or acetate may be substituted for rosaniline itself. Allow the solution to stand in a closed flask until it becomes colorless, or pale yellow. Then dilute it with 200 c.c. of water, and keep it in the dark in a tightly-stoppered bottle.

27. Chloral and Chloral Hydrate. How could chloral be prepared from acetaldehyde? from alcohol?

Put 10 g. of chloral hydrate in a distilling-flask, and treat it with 10 c.c. of pure concentrated sulphuric acid. Distill the chloral which results. Use a small iron crucible as an air-bath to heat the flask uniformly. Pass the vapors through a condenser, and collect the distillate in a small, dry distilling-flask protected by a calcium chloride tube which is attached to the side tube. Redistill the chloral, and determine its boiling-point.

a. Mix the chloral with water in the proportions of one gram-molecular weight of chloral to one gram-molecular weight of water.

b. Dissolve about one gram of chloral hydrate in a little water, and add to it a solution of sodium hydroxide. Identify the heavy liquid which separates. What does the alkaline solution contain? How could you test the accuracy of your conclusions?

c. By means of the tests which you have just employed to characterize aldehydes, can you show that chloral is an aldehyde?

Ketones.

★ **28. Acetone. Addition of Acid Sulphites.** Mix 10 c.c. of acetone with 15 c.c. of a cold *saturated* solution of sodium hydrogen sulphite. Shake the mixture for several minutes and cool it if necessary. What is the crystalline substance? Only ketones whose formulæ contain the group CH_3CO will respond to this test. Separate the crystals by filtration, and dry them on a piece of porous plate. Place this substance in a test-tube together with an equal weight of sodium carbonate and 5 c.c. of water. Heat the solution and observe the odor. Do aldehydes form similar addition products with sodium hydrogen sulphite? See acetaldehyde, formaldehyde, benzaldehyde. [R].

29. Condensation. Dibenzylidene Acetone, Dibenzalacetone. Put 5 drops of acetone, 1 c.c. of water, and 1 c.c. of benzaldehyde in a test-tube, and add 5 c.c. of strong alcohol and 1.5 c.c. of a 10 per cent. solution of sodium hydroxide. After mixing these substances, heat the mixture over a flame until it has boiled gently for one minute. Cool the liquid, and shake it until there is a separation of crystals, which may then be collected upon a small filter and washed with 5 c.c. of strong alcohol. Recrystallize the product from strong alcohol (5 c.c.); collect the crystals on a filter, wash them with 2 c.c. of alcohol, and dry them upon a piece of porous plate. The melting-point of dibenzylidene acetone is 112° . This test is sometimes employed to detect small amounts of acetone (e.g., in urine).

a. Treat a little benzalacetone with an excess of hydrochloric acid. In a similar way try concentrated hydriodic acid.*

30. Oxidation and Reduction of Acetone.

a. Does acetone reduce Fehling's solution or Tollen's solution? Does it color Schiff's reagent? [R].

b. What would be formed by the reduction of acetone? How is acetone prepared from calcium acetate? What would be formed if acetone were heated with dilute sulphuric acid and potassium permanganate? [R]. What relation does acetone bear to propane? How could it be converted into propane?

c. **Acetone from Isopropyl Alcohol by Oxidation.** Dissolve 0.5 g. of chromic anhydride (CrO_3) in 2 c.c. of water, and add

* Baeyer and Villiger, Ber. **35**, 1190 (1902); Thiele and Strauss, Ber. **36**, 2375 (1903).

0.3 c.c. of concentrated sulphuric acid. Put 6 drops of isopropyl alcohol in a small distilling-flask (15 c.c.), and cautiously add 0.5 c.c. of the chromic acid solutions to it. Cork the flask immediately, and incline it so that the side tube dips into a test-tube, and just below the surface of a solution containing 0.4 c.c. of water, 0.4 c.c. of benzaldehyde, and 2 c.c. of ethyl alcohol. Finally, heat the distilling-flask gently for a short time.

To the distillate collected in the test-tube, add 0.5 c.c. of a 10 per cent. solution of sodium hydroxide, and boil the mixture for about one minute. Recrystallize the dibenzylidene acetone from alcohol (1 c.c.). Collect the precipitate, dry it, and determine its melting-point (cf. § 29).

✕ **31. Acetoxime.** Dissolve 10 g. of hydroxylamine in 20 c.c. of water, and pour into it a solution of 5.8 g., one equivalent, of sodium hydroxide dissolved in 15 c.c. of water. Keep the hydroxylamine solution cold, and shake it while the alkaline solution, in small portions, is poured into it. Add 11 c.c. of acetone, and allow the mixture to stand for 24 hours. The oxime will separate as a white solid.

Collect the solid upon a Büchner funnel, and wash it once or twice with a little cold water. Extract the filtrate with ether, using about 20 c.c. Pour the ether extract through a dry filter-paper, and allow the ether to evaporate spontaneously. The total amount of solid obtained should be about 6 g. The oxime is quite volatile at room temperature, and should be preserved in closed vessels. It may be recrystallized from ligroïne which boils between 40° and 60°.

a. Carefully dry a small amount of recrystallized oxime in a desiccator, and determine its melting-point. Acetone is frequently identified by converting it into acetoxime.

b. What would be formed by reducing acetoxime, provided metallic sodium and alcohol were used as the reducing agent?

c. What significance do oximes have for the study of aldehydes and ketones? How could aldehydes and ketones be recovered from their respective oximes?

Note 5. — In this preparation, it is necessary to use sodium hydroxide and the hydroxylamine salt in equivalent amounts, since acetoxime cannot be extracted from an alkaline solution. (?) In many cases in preparing oximes, an excess, even three or four times the calculated amount of alkali, is essential. In other cases, however,

an acid solution must be used; e.g., quinone in hydrochloric acid gives a dioxime; in alkaline solution, it is reduced.

✓ **32. Hydrazones. Acetone Phenylhydrazone.** Dissolve 1 c.c. of freshly distilled phenylhydrazine in 0.5 c.c. of glacial acetic acid and 10 c.c. of water. Add 0.5 c.c. of acetone to 5 c.c. of water, and pour this solution into the phenylhydrazine solution. At first, a turbidity will result; and finally, an oil will separate. It may be extracted with ether. When the solution has been dried and the ether removed, acetone phenylhydrazone will be left as an oil.

Hydrazones are frequently employed to identify ketones and aldehydes. For this purpose, if phenylhydrazine does not yield solid crystalline hydrazones, it is the usual practice to choose some other hydrazine derivatives which will. Para-nitrophenylhydrazine and para-bromphenylhydrazine have been especially useful in this respect.

33. Acetone Para-nitrophenylhydrazone. Dissolve about 0.5 g. of para-nitrophenylhydrazine in 5 c.c. of glacial acetic acid and 10 c.c. of water. Pour this solution into 50 c.c. of water containing 4 drops of acetone. The mixture will become yellow and turbid; and, in the course of thirty minutes, the crystals will separate completely. After the para-nitrophenylhydrazone has been collected upon a filter and washed, drain it, and recrystallize it from a little hot alcohol. It forms golden-yellow crystals which melt at 148° . Because of the slight solubility of this hydrazone (.003 g. in 50 c.c. of water), it has been used to estimate acetone quantitatively, which can be done by drying and weighing the precipitated hydrazone. In this way, the distillate obtained from urine acidified with dilute sulphuric acid may be tested for acetone.



CHAPTER VI.

MONOBASIC FATTY ACIDS.

34. Formic Acid from Oxalic Acid. Heat 40 g. of glycerol in an open dish until a thermometer placed in the glycerol indicates a temperature of 175° . When the glycerol has been cooled, pour it into a distilling-flask which contains a weight of crystallized oxalic acid equal to that of the glycerol. Introduce a thermometer so that the bulb is surrounded by the glycerol, and distill the mixture until the thermometer registers a temperature of 150° . The distillate is essentially dilute formic acid. At this stage, cool the liquid in the distilling-flask to 50° , and add a second portion of oxalic acid (30 g.). The mixture may then be heated as before.

Place the combined fractions in a distilling-flask, and subject them to fractional distillation. Collect the fraction which boils between 105° and 108° . About what percentage of formic acid does this liquid contain? [R].

a. Salts of Formic Acid. After a portion of the acid solution has been made almost neutral by means of sodium hydroxide, evaporate it nearly to dryness, and allow the salt to crystallize.

b. To prepare the lead and copper salts, heat portions of the acid with the respective oxides, and filter the boiling solutions through small filter papers. Allow the filtrates to evaporate, and examine the salts which remain. Is the lead salt very soluble in cold water?

c. Reduction. Add a solution of silver nitrate to a little of the acid. To neutralize the acid add a slight excess of ammonia. Explain the change which takes place when the alkaline solution is warmed.

d. Make a solution of sodium formate, and add a few drops of mercuric chloride to it. Warm this solution gently. The white precipitate which separates is mercurous chloride, HgCl . Collect it upon a filter-paper and moisten it with ammonium hydroxide. It will turn black. Is this characteristic of mercur-

ous chloride? [R]. The formates are not the only substances which reduce mercuric chloride to mercurous chloride. Explain the reactions which take place when sodium formate reduces mercuric chloride. [R]. Would it be possible to construct an oxidation-reduction cell with sodium formate and mercuric chloride? Cf. § 22, Formaldehyde.

e. **Decomposition by Sulphuric Acid.** Heat a portion of the sodium salt with some concentrated sulphuric acid. What gas is evolved? Does it burn?

f. What relation does formic acid bear to formaldehyde? to methyl alcohol? to carbonic acid? to methane? How could you convert methyl alcohol and formaldehyde into formic acid?

g. Could formic acid be prepared by oxidizing methyl alcohol, if a mixture of sulphuric acid and potassium permanganate were used as the oxidizing agent? Could anhydrous formic acid be prepared by distilling a mixture of sodium formate and concentrated sulphuric acid?

h. What is the best way to prepare the anhydrous acid? [R]. Has formic anhydride ever been obtained? [R].

35. Formic Acid by the Oxidation of Methyl Alcohol. Make a mixture containing 30 c.c. of water, 10 c.c. of concentrated sulphuric acid, and 12 g. of powdered potassium dichromate. Cool the mixture thoroughly, and add 2.5 c.c. of methyl alcohol. After a few minutes, heat the mixture on a water-bath for fifteen minutes. Distill the product until the residue becomes thick.

Pour most of the distillate into a dish, and neutralize it by adding sodium carbonate to it. To make sure that the acid shall be in excess, add a few cubic centimeters of the distillate which have been kept in reserve for this purpose. Concentrate the salt solution until its volume is 10 c.c., and apply the characteristic tests for formic acid described in the previous preparation.

36. Acetic Acid. Place 25 g. of fused sodium acetate in a dry distilling-flask, and add to it 15 c.c. of pure concentrated sulphuric acid. Even if so-called "fused" sodium acetate is taken, it must be re-fused just before the experiment. It should not be heated much above its melting-point; it will decompose and turn dark if this is not guarded against. When the flask has been connected with a condenser, heat the mixture of salt

and acid on a sand-bath, and collect the distillate in a small, dry distilling-flask. Redistill the acid, and observe the boiling-point.

a. "**Glacial Acetic Acid.**" Pour a little of the fraction of highest boiling-point into a dry test-tube, and surround the tube with ice and salt. If the acid does not solidify at once, rub the walls of the tube with a stirring-rod.

b. **Salts and their Reactions.** Make a strong solution of sodium acetate. To one portion of the solution, add a solution of ferric chloride, and boil the deep-red liquid; to a second portion, add a solution of silver nitrate. Results? Does acetic acid reduce ammoniacal silver nitrate?

c. Dissolve a little pure sodium acetate in water and test the solution with neutral litmus paper. What is the reaction? How do you account for this? Make a concentrated solution of neutral soap, and add to it a few drops of phenolphthaleïn. Pour the mixture into a large volume of water. Explain the changes observed.

d. **Cacodylic Oxide.** [H]. Heat a small crystal of sodium acetate with a minute quantity of arsenious oxide. Cacodylic oxide is formed. It is extremely poisonous. Be very careful when noticing the odor. [R].

e. Is the vapor of acetic acid inflammable? Try to burn it.

f. What is sugar of lead? How is it prepared? What are the commercial sources of acetic acid?

g. Upon analysis, acetic acid and formaldehyde are found to have the same percentage composition: carbon, 39.78 per cent; hydrogen, 6.79 per cent.; oxygen, 53.43 per cent. Why do chemists assign the formula CH_2O to formaldehyde, and the formula $\text{C}_2\text{H}_4\text{O}_2$ to acetic acid? After you have collected the actual experimental data [R] by an inspection of the evidence for each, state the reasons in logical sequence.

CHAPTER VII.

DERIVATIVES OF FATTY ACIDS.

37. Methyl Ester of Formic Acid. Place 30 g. dry sodium formate in a small distilling-flask, and add to it a mixture of 10 g. of methyl alcohol and 32.5 c.c. pure, concentrated hydrochloric acid (sp. gr. 1.2). To prevent an increase in temperature, surround the flask with cold water, and add the acid and alcohol slowly. Close the flask air-tight, and allow the mixture to stand in a vessel of cold water for 24 hours; then distill the ester from a water-bath; and, in a receiver cooled by means of ice, collect all that passes over until the vapor reaches a temperature of 70°.

Keep the distillate cold, and add powdered calcium chloride to it as long as the solid dissolves. This usually causes the formation of two layers of liquid, which may be separated by means of a dropping-funnel. The upper layer, which is almost pure formic methyl ester, should be placed in a small flask, together with some solid calcium chloride. When the ester is dry, pour it into a distilling-flask, and distill it. The boiling-point of the ester is 32°.

a. Is the ester easily soluble in water?

b. Does it have an acid taste or odor?

c. What is the empirical formula of formic methyl ester? Compare this formula with the empirical formula of acetic acid. Compare the boiling-points, solubilities in water, and specific gravities [R] of the two compounds. Do they differ in their chemical behavior as well as in their physical properties?

d. How does the behavior of this ester towards sodium hydroxide differ from the behavior of acetic acid towards the same substance. [R]. How does this reaction help us in determining the constitutional formula to assign to formic methyl ester? What are the graphic formulæ of the two compounds? What name do we give to substances which bear this relation to one another? How do these formulæ represent the differences which

have been observed in the chemical behavior of the acid and the ester?

e. What acid bears the same relation to acetic methyl ester that acetic acid bears to formic methyl ester?

38. Acetic Ethyl Ester, Acetic Ether. In a distilling-flask, place a mixture of 20 c.c. of absolute alcohol and 25 c.c. of concentrated sulphuric acid. When the flask has been connected with a condenser, heat it on a wire gauze until a thermometer which reaches into the liquid indicates a temperature of 140° . The temperature must be kept between 140° and 145° during the process. Through a dropping-funnel, connected with the dropping-tube (cf. § 16, Diethyl Ether) which reaches to the bottom of the flask, allow a mixture of 25 c.c. of alcohol and 25 c.c. of glacial acetic acid to flow into the flask as rapidly as the ester distills into the receiver.

After you have transferred the distillate to a large beaker, cautiously add a solution of sodium carbonate, and stir the mixture until effervescence almost ceases. Why? Sometimes the effervescence is very slight.

By means of a separatory-funnel, separate the heavy layer from the lighter layer of acetic ether. Wash the ester several times with small portions of a strong solution of salt. Why? Distill the ester after it has been dried by means of porous calcium chloride. What is the boiling-point? [R]. What yield have you obtained?

39. Hydrolysis of the Ester. Put in a flask 5 c.c. of acetic ethyl ester, 2 g. of solid sodium hydroxide, and 50 c.c. of water. Connect the flask with a reflux-condenser and heat the alkaline solution for ten minutes. Then distill the solution until one-half of the liquid has passed over. What does the distillate contain? Empty the remainder of the alkaline solution into a porcelain dish, and evaporate it to dryness. What is this residue? Show by appropriate tests that your conclusions are correct?

a. Could dilute mineral acids be used to accelerate the hydrolysis of the ester? [R]. Are other esters affected in a similar manner by dilute acids and alkalis?

b. What influence would concentrated acetic acid have upon the completeness of the hydrolysis of the ester by water?

c. Compare the method used in the preparation of acetic

ethyl ester with that which was used to obtain diethyl ether. By equations and words, set forth any analogies which you may observe in the two processes, and any similarity in formulæ (type) of the ester and the ether.

d. Mention two other methods which may be used to prepare acetic ethyl ester, and show that these methods also have their analogies among the methods used to prepare diethyl ether. Are these methods general in their application?

e. There are two butyric acids which have the same empirical formula as acetic ethyl ester ($C_4H_8O_2$). Write the constitutional formulæ of these three substances, and tell how you could distinguish and identify each one by properly chosen experiments, chemical and physical. Are there any other esters of fatty acids which have this same empirical formula ($C_4H_8O_2$)?

f. In what respects does the action of sodium hydroxide upon acetic ethyl ester resemble the action of sodium hydroxide upon the fats and oils? What are soaps?

40. Acetyl Chloride. Place 25 g. of glacial acetic acid in a distilling-flask. A second distilling-flask, which serves as a receiver, should be joined to the condenser-tube by means of a sound cork. To absorb any hydrochloric acid which may be evolved, and at the same time to prevent moist air from entering the receiver, connect the side tube of the second distilling-flask with a long calcium chloride tube charged with soda-lime. Do not pack this tube too tight, and be careful that it does not stop up during the distillation.

By means of a dropping-funnel, allow 20 g. of phosphorus trichloride to run into the acetic acid, and at the same time prevent the mixture from becoming too warm by surrounding the flask with cold water. When all of the trichloride has been added, immerse the flask for fifteen minutes in a bath of water heated to 40° or 50° ; finally heat the water to boiling as long as the chloride distills. Redistill it, and observe the boiling-point. [R]. The yield varies from 20 to 25 g.

a. Mix a few drops of the chloride with a few drops of water. CARE! What gas escapes? What remains in the test-tube? How does the action of water upon acetyl chloride resemble the action of water upon phosphorus trichloride?

b. Gradually add 1 c.c. of acetyl chloride to 2 c.c. of absolute alcohol. Make the solution slightly alkaline, pour it upon a

watch-crystal, and notice the odor. What is formed? In what respect does this reaction resemble the action of acetyl chloride upon water?

41. Acetic Anhydride. When some "fused" sodium acetate has been re-fused, grind it to a fine powder, and put 20 g. of it into a distilling-flask. A condenser and a receiver similar to the ones used in the preparation of acetyl chloride should be used in this case also. After surrounding the flask by a bath of cold water, place 15 g. of acetyl chloride in a dropping-funnel; and, at intervals, allow one-half of this reagent to flow upon the acetate. To insure a thorough mixing of the two substances, remove the dropping-funnel, and stir the contents of the flask by means of a stout glass rod. The remainder of the chloride should then be added.

In order to complete the reaction, attach the flask to a reflux-condenser, and heat it in a bath of boiling water for twenty minutes. Then arrange the condenser in the position for distillation, and heat the flask in an oil-bath. Collect the acetic anhydride, and purify it by a second distillation. The boiling-point is about 138° . Approximately 20 g. should be obtained.

a. Mix a few drops of the anhydride with water. Does it react with water more readily, or less readily, than acetyl chloride? Does the water solution contain any hydrochloric acid? How could you detect it? What would its presence indicate? How would you treat the anhydride to eliminate this impurity?

b. Treat 1 c.c. of absolute alcohol with 1 c.c. of acetic anhydride, and warm the mixture gently. Add water to the product, and make it slightly alkaline. Pour it upon a watch-crystal, and notice the odor. What is formed?

c. How is acetic anhydride used to determine the "*presence*" of hydroxyl groups in organic compounds? to determine the "*number*" of hydroxyl groups? How may acetyl chloride or acetic anhydride be changed into ethyl alcohol?

d. Is there any method used to prepare ether which is analogous in principle to the methods which you have just employed in making acetic anhydride? By words and by graphic formulæ, point out any similarity in "*type*" which you may perceive when the formulæ of diethyl ether, acetic anhydride, and acetic ethyl ester are compared.

CHAPTER VIII.

SULPHUR COMPOUNDS.

42. Ethyl Mercaptan. Warm 2 c.c. of a saturated solution of potassium ethyl sulphate with 2 c.c. of a solution of potassium hydrogen sulphide (33 per cent.). Notice the odor of the mercaptan.

a. When subjected to oxidation, do the sulphur alcohols yield aldehydes and ketones?

b. Do sulphur alcohols give olefines and ethers when they are heated with concentrated sulphuric acid?

c. What is sulphonal? trional? tetronal? How is ethyl mercaptan used in their preparation?

43. Trimethylsulphonium Iodide. Dissolve 3 g. of potassium hydroxide in 30 c.c. of methyl alcohol. Pour the solution into a flask (about 200 c.c.), weigh the flask and contents to the nearest 0.1 g., and pass hydrogen sulphide into it until 0.8 g. has been absorbed.

Filter this solution into a somewhat smaller flask, connect it with a reflux-condenser, and add 5.5 c.c. of methyl iodide by pouring it in at the top of the condenser. Keep the mixture boiling gently for one-half hour.

While the solution is still warm, pour it out of the flask, leaving the solid potassium iodide behind. Trimethylsulphonium iodide will separate when this liquid has become cool. Recrystallize the salt from methyl alcohol.

a. Does a solution of this compound in water give silver iodide or silver sulphide when it is treated with a solution of silver nitrate? Explain.

b. How could you prepare the base to which this salt is related? Is it an active base?

CHAPTER IX.

COMPOUNDS CONTAINING NITROGEN.

44. Tests for Nitrogen in an Organic Compound. In most nitrogenous organic compounds, the nitrogen may be detected with the greatest certainty by the formation of sodium or potassium cyanide. To complete the test, convert the cyanide into Prussian-blue. The test is usually performed as follows: —

a. In a test-tube, heat to redness a few crystals of acetanilid with a *small* piece of sodium. [S.R.] Cool the fused mass, crush the test-tube in a dry mortar, and add 3 c.c. of alcohol. When the sodium has entirely dissolved, add water very cautiously. CARE! Boil the solution and filter it if necessary. After adding to the filtrate a drop of a solution of ferrous sulphate and one drop of a solution of ferric chloride, warm it gently, and acidify it with hydrochloric acid. (To make sure that the solution is acid, test it with litmus paper.) If the acid solution is distinctly blue, nitrogen is present. If it has a green color, allow it to stand for several hours; finally, a slight blue precipitate will form.

b. In a test-tube, heat several crystals of urea with a small quantity of soda-lime. What gas is evolved?

Amides.

45. Acetamide. Pour 50 g. of acetic ethyl ester into a flask containing 100 c.c. of strong ammonia-water (sp. gr. 0.90). When this mixture has become homogeneous, transfer it to a distilling-flask, and subject it to distillation. [H]. Put a few small pieces of porous plate into the flask to prevent "bumping," and heat the flask over a wire gauze. Keep the first fraction, and test it for alcohol. (?)

When the temperature indicated by the thermometer is about 170°, take away the condenser, and put in place of it a long, wide glass tube without a jacket; then continue the distillation, and collect in a beaker all that passes over between 175° and 230°. If the amide does not solidify when it has cooled, it will

crystallize if you rub the walls of the beaker with a stirring-rod. To remove the liquid which adheres to the crystals, collect them upon a Büchner funnel connected with a filter-flask and a pump, and press them upon a piece of porous plate. Acetamide boils at 223° . What yield have you obtained?

a. Recrystallize a small amount of acetamide with chloroform as the solvent. Determine the melting-point of the dry crystals.

b. Heat a few crystals with a strong solution of sodium hydroxide. Notice the odor. What gas is evolved?

c. Heat a little acetamide with dilute sulphuric acid, and observe the odor. What is formed? Explain *b* and *c*.

Nitriles.

46. Acetonitrile, Methyl Cyanide. Weigh out rapidly 10 to 15 g. of phosphorus pentoxide, and transfer it to a dry retort or to a distilling-flask. This can be done best by means of a wide cone made by twisting a smooth piece of writing paper. Add 10 g. of acetamide. By means of a thick glass rod, carefully mix these two substances thoroughly, and cover the mixture with a layer of 10 g. of phosphorus pentoxide.

When a condenser has been connected with the retort, slowly heat the retort, either in a bath of Wood's metal or with luminous flame. The heat should be applied in such a manner that undue foaming of the mass may be prevented as much as possible. Finally, increase the temperature until the nitrile slowly distills into the condenser.

Pour the distillate into one-half its volume of water, and shake the mixture. Powdered sodium hydroxide, added to the cold solution as long as it will dissolve, will cause the nitrile to separate as a lighter layer. It should be removed, dried with calcium chloride, and distilled over a little fresh phosphorus pentoxide. The boiling-point of acetonitrile is 81.6° .

a. Does the nitrile affect litmus?

b. Heat a small quantity of the nitrile with a solution of sodium hydroxide. What is the odor? Explain the result.

c. Could you prepare acetonitrile from ammonium acetate without previously isolating acetamide?

d. How are nitriles used to prepare organic acids? How could you pass from acetic acid to propionic acid by a series of reactions including this reaction?

e. By what experimental method could you change acetoni-trile into acetamide?

f. Isonitriles: Cf. Amines and Chloroform.

47. Ester of Nitrous Acid. Ethyl Nitrite. Dissolve 5 c.c. of ethyl alcohol and 10 g. of sodium nitrite in 50 c.c. of water. Pour this solution into a distilling-flask connected with a condenser and a receiver thoroughly cooled by means of ice. Heat the nitrite solution to a temperature of 20° – 25° . Make a solution containing 50 c.c. of water, 5 c.c. of concentrated sulphuric acid, and 5 c.c. of alcohol; pour it into a dropping-funnel, and allow it to flow slowly into the nitrite solution. Ethyl nitrite will distill. Its boiling-point is 17° .

a. What product, isomeric with ethyl nitrite, would be formed by the action of ethyl iodide upon silver nitrite? How could you distinguish them by the difference in their behavior towards reducing agents?

Nitroparaffines.

48. Nitroethane. What difficulties would you encounter in attempting to prepare nitroethane from ethane? Is it possible to obtain any nitroparaffines by the action of nitric acid on paraffine hydrocarbons?

The Sodium Salt of Nitroethane. Dissolve 0.5 g. of nitroethane in a little alcohol, and add to it a solution of sodium ethylate, made by allowing 0.2 g. of sodium to act upon a few cubic centimeters of ethyl alcohol. After transferring the precipitate to a filter, wash it with a little cold alcohol, and finally, with ether. When the salt has been dried, make the following tests: —

a. Heat a small piece of it on a spatula.

b. Dissolve some of the salt in the water. To one portion of the solution, add a solution of mercuric chloride; to a second portion, add bromine water.

c. Dissolve about one-half of the remaining salt in water, and add dilute sulphuric acid to it. What gas is evolved? Warm the solution, and observe the odor of the vapor which escapes. (?)

d. **Ethyl Nitrolic Acid.** Dissolve the remainder of the salt in water, and add to the solution a few crystals of sodium nitrite; acidify the solution slowly by adding dilute sulphuric acid; then add sodium hydroxide to it until it reacts alkaline. What

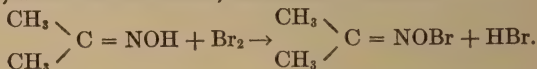
causes the solution to assume a red color? How could you isolate ethyl nitrolic acid? Is it a colored substance?

49. Pseudonitroles. Mix a little silver nitrite with an equal volume of dry sand, and transfer it to a small distilling-flask (15 c.c.) with a side tube about 20 cm. long. Pour 8–10 drops of isopropyl iodide upon the nitrite, and close the flask at once. When the sudden evolution of heat has moderated, distill the product over a small flame. No condenser need be used. Collect the distillate in a long test-tube, and shake it with three times its volume of a solution containing potassium nitrite and a little potassium hydroxide. Add dilute sulphuric acid, a drop at a time, until the solution reacts acid. Make it alkaline once more, and acidify it again. The blue color is caused by a pseudonitrole, which may be extracted by chloroform.

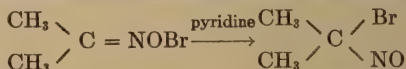
a. Cf. § 48, *c*, Nitroparaffines. Is the difference in behavior towards nitrous acid observed in these two cases characteristic of primary and secondary nitroparaffines in general?

50. Brom-nitrosopropane. To a dilute solution of acetone, add a few drops of a 10 per cent. solution of hydroxylamine hydrochloride and 1–2 drops of pyridine. Pour upon this solution about 1 c.c. of ether, and add bromine water gradually until the ether assumes a yellow color. When a few drops of a solution of hydrogen peroxide are added, and the mixture is shaken, the ether will assume a blue color. The color is caused by brom-nitrosopropane. (This reaction is employed to detect small quantities of acetone. Sensitiveness: 1 mg. in 5 c.c.)

The following equation expresses the course of the reaction. Acetoxime, which is first formed, reacts with bromine.



Pyridine accelerates the rearrangement of the compound.



Hydrogen peroxide disposes of impurities. (Piloty, Ber. **35**, 3099.)

Amines.

51. Methylamine from Acetamide. (For two students.)
Bromine must be handled with great care. Conduct the work

under a hood, and be careful not to breathe the bromine vapors or to spill any of the bromine on your hands. [Instructions!] Gradually add a cold solution of potassium hydroxide (25 g. of KOH in 100 c.c. water) to a mixture of 20 g. acetamide and 18 c.c. bromine (not bromine water). Keep this mixture cold while the potassium hydroxide is added, and stir it to prevent local heating. If a precipitate separates at this point, add a little water to dissolve it, and proceed. When the mixture assumes a pale-yellow color, place it in a dropping-funnel, and allow it to flow in a slow stream into a flask containing 60 g. of potassium hydroxide dissolved in 180 c.c. of water. The temperature of the alkaline solution in the flask should be kept between 60° and 70° ; it should not rise above 75° . Since considerable heat is evolved during the mixing of the solutions, it will be necessary to prevent overheating, by cooling the flask from time to time. During this part of the operation, and throughout the preparation, the flask should be connected with a condenser. The lower end of the condenser-tube should project into a receiver which contains a little ice-cold water, and should dip just below the surface of the water.

When the mixture has been kept at this temperature until the solution in the flask is practically colorless, the amine may be distilled. Put a few small pieces of clay-plate in the flask, place it upon a wire gauze, and, at first, heat it very gently with a small flame to prevent a sudden evolution of methyl amine gas, which, by its pressure, may burst the flask. The heat must be increased very gradually. Finally, boil the solution for several minutes until all of the amine has passed through the condenser.

a. Observe the odor of the solution collected in the receiver. Is it exactly like that of ammonia?

b. Does the solution have an alkaline reaction towards methyl-orange? towards litmus? For this test, make the methyl-orange and the litmus solutions slightly pink with acid, and divide each solution into two parts. To one part of each, add some of the amine solution; to the second part, add ammonium hydroxide solution. What do you conclude from the similarity in behavior?

c. Add some of the amine solution to a drop of copper sulphate solution, then, to a drop of aluminum sulphate solution. Repeat these tests, using ammonium hydroxide in place of the amine. Is there any similarity in behavior? Explain these reactions.

52. Methylammonium Chloride. After making these tests with the water solution, add dilute, pure hydrochloric acid to the cold amine solution until the liquid has a slight acid reaction. When the hydrochloric acid solution has been evaporated to dryness on a water-bath, the dry crystalline residue should be dissolved in the least possible amount of boiling absolute alcohol. In this process, use a small flask attached to an air condenser. A very small residue of ammonium chloride may remain undissolved at this point. If there should be a slight, insoluble residue, filter the solution, and evaporate the filtrate to dryness over a water-bath.

a. Heat a small amount of the solid hydrochloride with a solution of sodium hydroxide. Notice the odor. What gas escapes?

b. Warm some of the salt with calcium oxide in a small, dry test-tube. Is the gas which escapes inflammable? Test the vapor with litmus paper.

c. Try the same tests with ammonium chloride in place of methylammonium chloride. Write all equations necessary to emphasize the similarity in the two cases.

d. **Chlorplatinate.** Dissolve some of the salt in a little alcohol, and add to it a few drops of a 10 per cent. solution of platinic chloride. If no precipitate appears, add a few drops of ether to this solution. What is formed? [R]. To one drop of a solution of ammonium chloride, add a drop of platinic chloride solution. Compare the precipitates formed in the two cases.

e. **Isocyanide Reaction for Primary Amines.** [H]. Place a few crystals of the hydrochloride in a test-tube with two or three drops of chloroform; add 1 or 2 c.c. of a solution of potassium hydroxide in alcohol, and warm the mixture under the hood. The isocyanide can be recognized in small amounts by its odor. It is poisonous. When you have finished the test, pour the contents of the test-tube into the hood-sink, and rinse out the tube with concentrated hydrochloric acid before you take it to your desk. Is it possible to prepare a salt of hydrogen isocyanide by heating ammonia with alcohol potash and chloroform? [R].

53. Triethylammonium Bromide from Diethylamine. In a small flask, mix 5 g. of diethylamine and 8 g. of ethyl bromide. Allow the mixture to stand one day. Connect the flask with a

reflux-condenser, and heat it for a few minutes upon a water-bath. Cool the reaction product, collect the crystals upon a filter, and dry them carefully.

a. With this salt in place of methylammonium chloride, try the test described under § 52, *a-e*.

54. Triethylamine. Place the triethylammonium bromide in a small, dry distilling-flask connected with a condenser, and add to it 4 g. of powdered potassium hydroxide. Heat the flask in a bath of boiling water, and collect the amine in a cool receiver. Determine the boiling-point of the amine.

a. Dissolve a few drops of triethylamine in water and apply the tests described under § 51 *a-c*.

55. Tetraethylammonium Bromide. Weigh the triethylamine just obtained and mix it with the calculated amount (one gram equivalent) of ethyl bromide. In the course of a day, long needles of tetraethylammonium bromide will separate.

a. What is the base to which this salt is related? How would you prepare it from the bromide? Is it an active base? [R].

DIVISION 2. POLYATOMIC COMPOUNDS.



CHAPTER X.

HALOGEN COMPOUNDS.

56. Ethylene Dibromides. Pour a mixture of 25 g. of absolute alcohol and 150 g. of pure concentrated sulphuric acid into a 2-liter flask. Support the flask over a wire gauze, and close it with a stopper having two openings. Through one opening, insert a long-stemmed dropping-funnel; through the other, a doubly-bent delivery-tube leading to the first of a train of three wash-bottles. Charge the first wash-bottle with concentrated sulphuric acid; the second with a strong solution of sodium hydroxide. The third wash-bottle should contain 40 g. of bromine, covered with a layer of water, and should be placed in a vessel of cold water.

Heat the flask cautiously until a regular evolution of gas begins; then, through the dropping-funnel, introduce a mixture of one part of alcohol and two parts of concentrated sulphuric acid. This mixture should be added fast enough to furnish a constant stream of gas; at the same time, violent foaming of the charge should be avoided. When the bromine has changed completely into a transparent, almost colorless liquid, transfer the contents of the absorption bottle to a separatory-funnel, and wash the heavy oil first with a dilute solution of sodium hydroxide, and then with water. Why? Separate the oil, and dry it with calcium chloride for several hours. Distill it, and preserve it for the preparation of glycol. (Cf. § 59.)

Note 6. — A mixture of 50 c.c. of phosphoric acid (sp. gr. 1.7) and 25 c.c. of alcohol may be substituted for the sulphuric acid and alcohol. If alcohol is run into this mixture, heated to about 200°, a constant stream of ethylene will be obtained without the foaming so objectionable when sulphuric acid is employed.

57. Chloroform. Select a 2-liter flask and fit it with a stopper which has two openings. Through one of the openings insert a bent tube which serves to connect the flask with a con-

denser; through the second, introduce a tube long enough to reach to the bottom of the flask, and arranged so that steam may be conducted through it. The tube which reaches to the bottom of the flask *must be wide* in order to avoid stoppage; a straight calcium chloride tube, or a dropping-tube, will answer.

To generate a current of steam, use a 1-liter flask * with a stopper which has two openings, one for an exit tube, and the other for a glass tube, two or three feet long, which serves as a safety-valve. Place the contents of two half-pound boxes of bleaching-powder and 700 c.c. of water in the 2-liter flask. Slowly add a mixture of 25 c.c. of acetone and 50 c.c. of water; shake the flask frequently during the addition, and cool it at once if the mixture becomes decidedly warm. Finally, support the flask upon a tripod covered by a piece of wire gauze, and

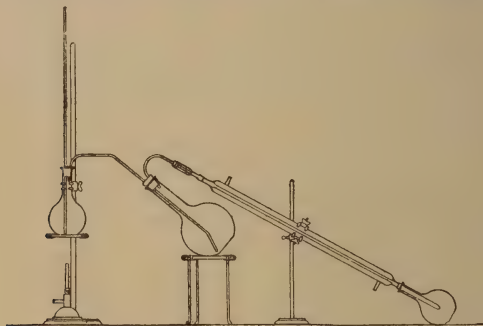


Fig. 16. Steam Distillation.

connect it on the one side with the condenser and on the other side with the steam generator.

When these connections have been made, heat the contents of the 2-liter flask until the liquid in it is near the boiling-point, pass a rapid current of steam into the flask, and drive the chloroform into the condenser. Collect all of the distillate until you can see no more globules of oil in the liquid as it drops from the end of the condenser.

To purify the chloroform, shake it several times in a separatory-funnel with a saturated solution of salt. Why? Dry it

* A tin ether can may be used in place of a glass flask.

with fused calcium chloride, and distill it. At what temperature does pure chloroform boil? [R]. What yield of chloroform have you obtained?

a. Try to burn a little of the chloroform.

b. Warm two or three drops of chloroform with a crystal of potassium dichromate and a small amount of concentrated sulphuric acid. Observe the odor of the vapors which escape. What changes take place in moist chloroform when it is exposed to air and light? [R].

c. **Isonitrile Reaction.** [H]. Warm one drop of water solution of aniline with a drop of chloroform and a little alcoholic potash. Perform the experiment *under the hood*; empty the liquid into the sink under the hood, and wash the test-tube with concentrated hydrochloric acid before you take it to your desk. To what class of amines does aniline belong? Cf. § 51, Methylamine.

d. What substances would be produced by heating chloroform with alcoholic potash?

e. Add a small crystal of iodine to some chloroform.

f. What methods are employed to prepare pure chloroform for use as an anæsthetic?

58. Iodoform. Put into a small flask 10 g. of anhydrous sodium carbonate, and dissolve it in 60 c.c. of warm water. Add 8 c.c. of alcohol to this solution, immerse the flask in a water-bath, and heat the liquid to a temperature between 70° and 80°; then add gradually 6 g. of powdered iodine. If the solution has a brown color when it has been heated for a few minutes, add a solution of sodium carbonate, drop by drop, until the brown color just disappears. Cool the liquid, collect the iodoform upon a small filter, and wash it with water. When the solid has drained, recrystallize it from alcohol as follows.

After sufficient alcohol has been used to dissolve all of the yellow precipitate, filter the hot solution rapidly through a small paper, which will remove insoluble impurities, chiefly unchanged sodium carbonate; and add water to the filtrate until the iodoform is completely precipitated as a yellow crystalline deposit. Cool the mixture, and collect the precipitate upon a small filter. When the recrystallized iodoform has been dried, preferably upon a small piece of porous plate, determine its melting-point.

CHAPTER XI.

POLYATOMIC ALCOHOLS AND DIKETONES.

59. Ethylene Glycol. In a flask connected with a reflux-condenser, heat 40 g. of ethylene dibromide with 28 g. of anhydrous potassium carbonate and 250 c.c. of water, until the ethylene dibromide has disappeared. This operation will require some 10–12 hours. To prevent "bumping," place in the flask several long pine splinters. When the oily dibromide has disappeared, remove the water by evaporation. Owing to the volatility of the glycol with steam, there will be less loss of glycol if the solution is concentrated under diminished pressure.

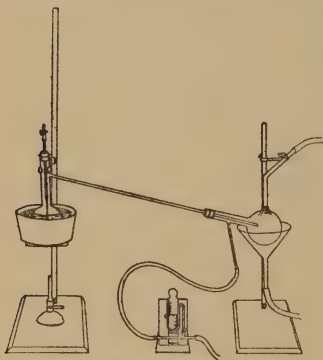


Fig. 17. Distillation in vacuo.

Two distilling-flasks should be connected air-tight by means of rubber stoppers. Through the stopper of the distilling-flask proper, insert a glass tube drawn out to a wide capillary. The tip of this capillary must nearly touch the bottom of the flask; and at all times during the distillation, it should dip below the surface of the liquid. A piece of rubber tubing and a screw-clamp attached to the upper end of the glass tube will make it possible to regulate the amount of air admitted. The constant formation of air bubbles at the lower end of the capillary will prevent the "bumping" of the boiling liquid. When it is desirable to know the temperature at which a given substance is distilling, a thermometer may be placed inside this glass tube with its bulb resting on the shoulders where the capillary begins, and with its upper end just below the clamp, so that by removing

the clamp and the rubber tube, the thermometer may be taken out easily.

The flask which serves as a receiver, may be cooled if desired. In some cases it is necessary to insert a short condenser between the two flasks to insure sufficient cooling. A filter-pump will give the desired diminution of pressure. When the pressure under which a substance is distilling is to be determined, a manometer (cf. illustration) should be inserted between the receiving flask and the pump.* In the preparation of glycol, since only the solvent is distilling, no thermometer or manometer will be needed.

When most of the water has distilled and a considerable amount of salt has separated, treat the residue with alcohol to extract the glycol from the crystals of potassium bromide. When the alcohol has been removed by distillation in vacuo, distill the residual glycol at atmospheric pressure. The fraction which boils between 170°–200° will be practically pure glycol. About 4–5 g. will be obtained. The boiling-point of pure glycol is 197.5°.

a. What would the theoretical amount of glycol be? How do you account for this loss? Are any other products formed? What would be the chief product if ethylene dibromide were heated with alcoholic potash? How could you verify your conclusions experimentally? Try your method.

b. Treat a little glycol with a piece of metallic sodium. Explain your result.

c. Taste a drop of glycol.

d. Glycol is a diprimary alcohol. What are its oxidation products?

e. What is ethylene oxide? Would you call it an ether? Is the method by which ethylene oxide is usually made similar to any method used to prepare dimethyl ether?

60. The Glycol Ester of Benzoic Acid. In a test-tube, mix 2 drops of glycol, 0.2 c.c. of benzoyl chloride, and 5 c.c. of a 10 per cent. solution of sodium hydroxide. Close the test-tube and shake it for several minutes. After adding 10 c.c. of water, shake the tube again, and collect the precipitate upon a filter. Wash this precipitate, dissolve it in about 25 c.c. of dilute alcohol (1 : 1), and filter the hot solution to remove any suspended

* Concerning special forms of apparatus used in fractional distillation under diminished pressure, consult reference books.

particles. Collect the precipitate which forms in the cold solution, wash it with 5 c.c. of dilute alcohol (1 : 1), dry it, and determine its melting-point. It should melt at 70°–71°. Cf. §§ 11, 12, 40 *b*, Schotten-Baumann's reaction.

61. Glycerol.

a. Add two or three drops of a dilute solution of copper sulphate to a solution of glycerol. Make this solution slightly alkaline by adding a solution of sodium hydroxide. Does a precipitate form? How do you explain the sudden change in color? Add a solution of sodium hydroxide to a dilute solution of copper sulphate containing no glycerol. What difference do you observe?

b. Glycerol Ester of Benzoic Acid. Dissolve 4 drops of glycerol in 10 c.c. of a 10 per cent. solution of sodium hydroxide contained in a small flask, and add 1 c.c. of benzoyl chloride. Close the flask, and shake it vigorously for several minutes, until a curdy precipitate has formed. It may be necessary to cool the flask from time to time. Add 10 c.c. of water and shake the flask again for a few seconds. Collect the precipitate upon a filter, wash it with water, and then with 10 c.c. of dilute acetic acid? Why?

Finally, dissolve it in 15 c.c. of boiling alcohol (2 parts alcohol to 1 part water), filter the solution, cool the filtrate, and shake it until the ester is precipitated. Collect the precipitate upon a filter, wash it with 3 c.c. of dilute alcohol (2 : 1), dry it, and determine the melting-point. The pure ester melts at 70°–72°. Cf. § 11, Ethyl Alcohol; § 60, Glycol Ester.

c. What are the chief constituents of the fats? In what respects are they related chemically to the ester of benzoic acid made in *b*? How is glycerol obtained from the fats? What is lipase, and how does it act in decomposing and in synthesizing fats?

d. How is "nitroglycerine" made? Why is the name "nitroglycerine" chemically a misnomer?

*e. Acrolein from Glycerol.** Put 1 g. of glycerol and 0.1 g. of phosphoric acid (sp. gr. 1.7) in a dry test-tube. Close the tube

* *Note 7.*—Powdered fused potassium acid sulphate may be substituted for phosphoric acid; it is objectionable because of the violent foaming of the mixture which it causes. The method given above was proposed by Nef, *Ann.* **335**, 221 (note).



with a stopper which has a bent delivery tube some 20 cm. long. The end of this tube should dip beneath the surface of 2 c.c. of water in a small test-tube. Heat the glycerol for a few minutes at a temperature of about 240° . Filter the water solution, and apply the following reagents: — Fehling's solution; ammoniacal silver nitrate; Schiff's reagent.

α -Diketone Derivatives.

62. Nickel Salt of Dimethylglyoxime. Put one drop of a solution of nickel nitrate or chloride (10 per cent.) in a large test-tube; fill the tube with distilled water, and mix the liquids thoroughly. Pour one drop of this solution upon a few crystals of dimethylglyoxime, and make this mixture faintly alkaline by adding a little very dilute ammonium hydroxide. The red substance which forms is a nickel salt of dimethylglyoxime, $C_8H_{18}N_4O_4Ni$. This reaction furnishes a most delicate test for the presence of a nickel salt. It may be used to detect nickel in the presence of a large amount of cobalt; e.g., in commercial cobalt salts.

β -Diketones.

63. Acetylacetone.

a. To a dilute solution of acetylacetone in water, add a drop or two of a dilute solution of ferric chloride. Explain the change which occurs.

b. To a solution containing 1 g. of copper acetate in 25 c.c. of water, add 0.5 g. of acetylacetone. A blue copper salt of acetylacetone, almost insoluble in water, will separate readily. When the mixture has been shaken until there is no further increase in the volume of precipitate, collect the copper salt upon a filter, wash it with water, and dry it. Dissolve the dry salt in some boiling chloroform. Add hot alcohol until a precipitate commences to form and allow the salt to crystallize slowly from this solvent. Collect the crystals, wash them with alcohol, and dry them. The melting-point is 230° .

c. Heat some dry crystals of the copper salt in a dry test-tube. If heat is applied gently, a green vapor will form, and the salt will sublime and deposit in bright blue needles. If the heat is too great, copper will be deposited.

CHAPTER XII.

DIBASIC ACIDS.

64. Oxalic Acid. Heat 1 g. of dry sodium formate in a small test-tube. When the salt melts, does it boil, or is a gas evolved as a result of decomposition? Apply a flame to the mouth of the test-tube. Cool the fused mass, dissolve it in water, and add a few drops of a solution of calcium chloride and a little acetic acid. (?) Dissolve some unchanged sodium formate in water, and treat the solution with calcium chloride and acetic acid. Does a precipitate form in this case also? Explain your observations.

a. Calcium Salt. Neutralize a solution of oxalic acid by means of ammonium hydroxide. Add a solution of calcium chloride. Is the precipitate soluble in acetic acid? What use is made of this salt in detecting small amounts of calcium, and in estimating calcium quantitatively? What other salts of calcium are soluble with difficulty in acetic acid?

b. Heat a few crystals of oxalic acid, or an oxalate, with some concentrated sulphuric acid. What change occurs? What gases are evolved? Make appropriate tests for each gas.

65. Complex Oxalate Ions.

a. Make a 10 per cent. solution of ammonium ferric sulphate, of potassium ferricoxalate, and of potassium ferricyanide. Test small samples of each solution with sodium hydroxide. Which solutions yield precipitates? Explain.

b. Pour 5 c.c. of each of the three solutions into separate test-tubes. Place the tubes side by side, and add to each 3 drops of a 10 per cent. solution of potassium thiocyanate. Under these conditions, this reagent serves as a test for ferric ions in the case of ammonium ferric sulphate only. The complex ferricoxalate ion is slightly dissociated (cf. *a*), but has a rather large "stability constant."



This can be demonstrated experimentally as follows: —

α. To 5 c.c. of potassium ferricoxalate solution, add three drops of the potassium sulphocyanate solution and several drops of dilute hydrochloric acid. Explain the appearance of the red color.

To 5 c.c. of the ferricoxalate solution, add three drops of potassium sulphocyanate, and a little calcium chloride. How do you explain the appearance of the red color?

β. To 5 c.c. of the ferricoxalate solution, add 1 c.c. of calcium chloride solution (10 per cent.). Calcium oxalate is precipitated.

To 5 c.c. of ferricoxalate solution, add a small piece of solid ferric chloride about the size of a pea. After it has dissolved, add 1 c.c. of the calcium chloride solution. Is any calcium oxalate precipitated? Explain the difference in behavior in these two cases.

c. Interpret these results (*a* and *b*) in terms of the law of mass action and of chemical equilibrium as applied to the dissociation of the complex ferricoxalate ion. What are double salts, and how are they distinguished from salts of complex acids? How would you classify the three iron salts used in *a*?

66. Oxalic Acid as a Reducing Agent.

a. Mix a crystal of oxalic acid, or an oxalate, with some powdered manganese dioxide and a little dilute sulphuric acid. What gas is evolved? Corroborate your conclusion by an appropriate test.

b. Add a few drops of a dilute solution of potassium permanganate to a warm solution of oxalic acid containing some dilute sulphuric acid. By equations, represent the reaction involved in the change.

c. Action of Light in Accelerating Reduction. Make a solution of mercuric chloride containing 0.5 g. in 10 c.c. of water. Prepare a second solution containing 0.8 g. of ammonium oxalate in 20 c.c. of water. Mix these two solutions, and divide the mixed solution, placing 15 c.c. in each of two test-tubes. Put one of these tubes in the sunlight, and the other in a dark cupboard of the desk. In the course of a few minutes, the tube in the light will become turbid; and, after a short time, a white precipitate will form. What is it? Represent the changes by equations. The tube in the dark will show no change even after several days. How could this reaction be employed to measure the relative intensities of light from different sources? In the case of the

oxalates of iron, how is this principle put to practical use in photography?

67. Malonic Acid. Place 20 g. of monochloroacetic acid in a porcelain dish containing 40 c.c. of water. Neutralize the acid by adding the calculated amount of sodium acid carbonate. Heat the mixture to 50° or 60° until effervescence ceases; then add 16 g. of powdered potassium cyanide. Potassium cyanide must be handled with great care. This operation must be carried out under the hood. Precautions must be taken not to breathe the vapors which escape; they may contain prussic acid and, if so, are very poisonous. After adding the cyanide, stir the mixture, and apply a gentle heat until the reaction is complete.

After heating the solution for half an hour, add a solution of sodium hydroxide containing 16 g. of hydroxide in 40 c.c. of water. Boil the alkaline solution until ammonia ceases to be evolved. Add enough water to replace that which passes away by evaporation. Finally, neutralize the solution by adding slowly that amount of dilute hydrochloric acid which contains 7 g. of hydrogen chloride. How can this value be calculated? To precipitate the malonic acid, add a solution of calcium chloride (30 g.). Filter the calcium malonate, wash it with a little cold water, and dry it at 100° until the weight is practically constant.

To obtain malonic acid, treat a weighed quantity of the dry calcium salt with a strong solution of oxalic acid containing the calculated amount of oxalic acid. After warming the mixture for a short time, filter it, and evaporate the filtrate over a water-bath.

a. Determine the melting-point of the malonic acid which you have made.

b. Heat some malonic acid in a test-tube. What gas is evolved? What remains in the tube?

c. In a distilling-flask with a long neck, heat 1 g. of ethyl malonic acid. What gas is evolved? When the fused acid has been heated (160° – 170°) until gas evolution has ceased, distill the remaining liquid, and observe the boiling-point. By appropriate tests, determine what this substance is.

d. How can the esters of malonic acid be prepared? What use is made of malonic ethyl ester in the synthesis of acids of the acetic acid series?

68. Fumaric Acid from Maleïc Acid. Rearrangement of Stereoisomers. Dissolve 0.4 g. of maleïc acid in 1 c.c. of water, and add a drop or two of bromine to the solution. Divide it into two parts. Place one part in the dark and the other in direct sunlight. In the course of a few minutes, the tube placed in the light will be found to contain a solution turbid with suspended fumaric acid. In the dark, even after many hours, no fumaric acid will separate.

a. What is maleïc anhydride? Does fumaric acid yield an anhydride? [R].

b. What explanation is offered to account for these two isomers? How are their space formulæ chosen?

c. How can fumaric acid be converted into maleïc acid?

d. Add a few drops of an alkaline solution of potassium permanganate to a solution of maleïc acid. (?)

CHAPTER XIII.

CYANOGEN AND RELATED COMPOUNDS.

69. Cyanogen, Dicyanogen. Heat a small quantity of mercuric cyanide in a dry test-tube, and kindle the gas which escapes from the tube. What relation does cyanogen bear to oxalic acid? [R].

70. Salts of Hydrocyanic Acid or Prussic Acid.

a. Mercuric Cyanide. Dissolve a little mercuric cyanide in water, and add it to a solution of silver nitrate. Try the same test, using potassium cyanide instead of mercuric cyanide. Explain your observations.

b. Potassium Ferrocyanide. Dissolve 3.5 g. of ferrous sulphate in 50 c.c. of water. Add 5 g. of potassium cyanide, and boil the solution for a short time. Filter the solution, and evaporate the filtrate on a water-bath until the salt commences to crystallize. When the salt has crystallized from the cold solution, collect it, and test it. (?)

c. How would you convert potassium ferrocyanide into potassium ferricyanide? How is potassium cyanide made from potassium ferrocyanide? What is the technical process employed in the making of potassium ferrocyanide? How is Prussian blue made?

d. How are alkyl cyanides and alkyl isocyanides related to prussic acid? When they are hydrolyzed in the presence of dilute mineral acids, what products do they yield? In what respects does the behavior of these alkyl derivatives differ from that which would naturally be suggested for them by analogy through a study of the hydrolysis of such compounds as acetic ethyl ester, ethyl nitrite, and ethyl sulphate? From the viewpoint of structure chemistry, and in the language of structural formulæ, can you propose any hypothesis to account for this divergence?

71. Cyanic Acid and the Cyanates. Heat a strong solution of potassium cyanate (not cyanide) with a little sodium hydrox-

ide. Test the vapors with a piece of neutral litmus paper, and notice the odor. Add acid to the remaining solution. What gas is evolved?

a. What relation does cyanic acid bear to carbonic acid? Can you illustrate this relation by appropriate graphic formulæ? What compound bears a similar relation to acetic acid? How can potassium cyanide be converted into potassium cyanate?

72. Methyl Isocyanate. Make a dry mixture of potassium cyanate and sodium methyl sulphate, and heat it in a dry test-tube. Observe the odor. What products would be obtained by the hydrolysis of methyl isocyanate? (Würtz method of making primary amines). Cf. § 70, *d*.

73. Cyanic Acid from Cyanuric Acid. In a small distilling-flask with a long side tube, place several grams of cyanuric acid, previously dehydrated in a beaker upon a water-bath.

Dip the side tube of the flask into a long test-tube surrounded by a freezing-mixture, and heat the bulb until the cyanuric acid has almost disappeared. A colorless liquid will be obtained in the test-tube. Notice the odor of this liquid. Test a drop of it with moist litmus paper. When the liquid becomes warm by standing at room temperature, it will suddenly polymerize with a decrepitating sound, and will change to a mixture of cyanuric acid and cyamelid. [R].

Thiocyanic Acid and Isothiocyanic Acid.

74. Ammonium Thiocyanate. Mix 3 c.c. of carbon disulphide with 15 c.c. of concentrated ammonia water, and add to the mixture 15 c.c. of alcohol. After two days, evaporate the solution to dryness over a water-bath. Extract the thiocyanate from the residue by means of hot alcohol. Filter the solution, and allow the salt to crystallize from the alcohol. Dry the salt upon a piece of porous plate, and make tests to show that it is a thiocyanate.

75. Methyl Thiocyanate. Dimethyl Sulphate as an Alkylating Agent. [H]. Dissolve 20 g. of potassium thiocyanate in 10 c.c. of water. To the cold mixture, add, in two portions, 26 g. of dimethyl sulphate. Dimethyl sulphate is extremely poisonous and has no odor. Exercise great care in working with it. Shake the mixture thoroughly and cool it if necessary. After the solution has been heated 15 minutes upon a water-bath, and has been shaken repeatedly during this time, pour the

liquid into a separatory-funnel, and remove the ester which will accumulate as a lighter layer. Dry it with calcium chloride, and distill it. The yield should be about 10 g. The ester thus obtained will boil between 130° – 133° .

a. What evidence is there to show that a formula in which the methyl group is linked to sulphur represents the chemical behavior of this ester in a satisfactory manner?

76. Methyl Mustard-Oil. (Hofmann's reaction.) Place a few crystals of methylammonium chloride in a test-tube, and pour upon them several drops of alcohol, 1 drop of carbon disulphide, and 1 or 2 drops of a strong solution of potassium hydroxide. After a few seconds, add a little water and a slight excess of a dilute solution of silver nitrate. When the solution is warmed until it boils, the odor of the mustard-oil will become pronounced. What are the intermediate products in this reaction? Explain their conversion into methyl mustard-oil.

a. What class of amines may be used in making mustard-oils by this method?

b. What experimental evidence [R] can you mention to justify the linking of the alkyl groups to nitrogen in the graphic formulæ assigned to mustard-oils? Cf. § 72, Methyl Isocyanate.

CHAPTER XIV.

UREA AND UREIDS.

77. Urea. (Wöhler's Synthesis.) Mix a solution of 10 g. of potassium cyanate with a solution of 20 g. of ammonium sulphate in 25 g. of water; place the mixture in a porcelain dish, and evaporate it to dryness over a water-bath. Powder the dry residue, and place it in a small, dry flask connected with a tube which serves as an air-condenser. Add 15 c.c. of absolute alcohol, and heat the flask on a water-bath until the alcohol boils. Pour the hot alcohol through a small filter, leaving the residue in the flask. After repeating this treatment with alcohol three times, combine the filtrates, place them in an evaporating dish, and evaporate them to dryness. Determine the melting-point of the dry crystals. What is the melting-point of urea?

78. Urea from Phosgene. Pour 15 c.c. of ammonia water (sp. gr. 0.96) into a small flask, and add to it slowly 10 c.c. of a 20 per cent. solution of phosgene in toluene. [H]. Shake the flask and cool it if necessary. The solution must react alkaline when all of the phosgene has been added. Evaporate the solution, and extract the urea as described in § 77.

These tests are to be performed either with § 77 or with § 78.

a. Boil a little urea with a strong solution of sodium hydroxide. What gas is evolved? Acidify the alkaline solution by adding hydrochloric acid, drop by drop. What gas is liberated? How do you explain these changes? In what respects does urea resemble acetamide? How can you express the relation which it bears to ammonia? to carbonic acid?

b. Make a strong solution of urea, about 1 c.c., and add some pure concentrated nitric acid to it. What is formed? How is it possible to obtain urea from this substance? How will a solution of ammonia in water react with nitric acid? When you take this fact into consideration, what is the probable action of nitric acid upon the urea in water solution?

c. Add bromine to a solution of sodium hydroxide until the solution has a deep-yellow color (not red). Fill a test-tube with

this solution, and invert it in a dish containing some of the same solution. Put 0.5 g. of urea under the test-tube. What gas is formed? How is this method employed to estimate urea quantitatively? How would the same reagent act upon ammonia?

d. Describe one method by which urea could be made synthetically if you had only carbon, oxygen, chlorine, nitrogen, and hydrogen to begin with. Write all equations necessary to illustrate the experimental steps.

e. What is the significance of the terms ureïds and diureïds?

79. Biuret and Cyanuric Acid from Urea. Heat one gram of urea in a test-tube until the substance melts and evolves a gas. Notice the odor of the gas, and test it with moist neutral litmus paper. When the evolution of gas has almost ceased, and the fused mass has become thick, cool the tube, and digest the residue with 3 c.c. of cold water.

a. **Biuret** will dissolve, and may be detected by the addition of a few drops of a solution of potassium hydroxide and one or two drops of a 10 per cent. solution of copper sulphate. Violet-red copper biuret will be produced. This is one of the most delicate tests for urea. In what sense is biuret related to a ureïd?

b. **Cyanuric acid** forms the chief product in the tube. After washing the residue once more with 5 c.c. of cold water, dissolve the remaining solid in a few cubic centimeters of boiling water, cool the solution, and add a cubic centimeter of an ammoniacal solution of copper sulphate. Copper cyanurate will separate as a violet crystalline powder.

80. Murexid. Mix 0.5 g. of uric acid with one cubic centimeter of concentrated nitric acid (sp. gr. 1.4), place the mixture in a porcelain dish, and evaporate the solution nearly to dryness. Cautiously add a dilute solution of ammonia. The ammonium salt of purpuric acid (murexid test) will be formed as a purple-red dye. Try the same reaction, substituting caffeine for uric acid. Is a similar product formed in this case?

CHAPTER XV.

POLYATOMIC COMPOUNDS WITH MIXED FUNCTIONS.

81. Monochlor Acetic Acid. *Caution:—Do not get this acid on your hands; it produces severe burns.* Pour 40 g. of glacial acetic acid into a flask containing 6 g. of red phosphorus. Through the stopper of the flask, insert a delivery-tube and the end of a reflux-condenser. When the flask has been heated in a bath of boiling water, conduct a rapid current of dry chlorine gas into the acid. The absorption of chlorine will take place quite rapidly if the operation is performed in the direct sunlight. If it is impossible to arrange the apparatus so that the direct sunlight can fall upon it, the same result may be brought about somewhat more slowly if a mirror is used to reflect the sunlight upon the flask. The reaction will be complete when a portion of the chlorinated product, placed in a test-tube, solidifies on being cooled with ice.

Transfer the crude product to a distilling-flask, and distill it. Allow the vapors to pass through a long "air condenser," and collect two fractions. The portion which distills between 150° and 200° will be chiefly monochlor acetic acid. This fraction will crystallize when it has been cooled in a beaker surrounded by ice. Transfer the crystals to a Büchner funnel; and, with the aid of a pump, separate the liquid from the crystals as rapidly as possible. The monochloride may fuse if suction is applied too long. A second fraction, boiling between 150° and 200° , may be obtained by distilling the liquid filtered from the crystals.

The crystals collected in this way should be distilled again. About 25 g. of monochlor acetic acid will be obtained. The boiling-point of the acid is about 186° .

a. After finding an appropriate solvent, recrystallize a portion of the acid. Determine the melting-point of the pure, dry substance.

b. Dissolve some of the recrystallized acid in a little water. To one portion of this solution, add a solution of silver nitrate.

Is any silver chloride formed? To a second portion of the solution add enough sodium carbonate to neutralize the acid. Boil the solution for a few minutes. Add some dilute nitric acid, and then some silver nitrate. What are the products formed by boiling monochloroacetic acid with dilute alkalis?

c. Why is phosphorus used in the chlorination of acetic acid? What substances may be used in place of phosphorus? What other organic compounds are formed during the preparation of monochloroacetic acid?

Alcohol Acids.

82. Lactic Acid. Distill 5 c.c. of lactic acid with 15 c.c. of 30 per cent. sulphuric acid at 130° . Collect the distillate in a cold receiver, and without applying heat test one portion for acetaldehyde by means of an ammoniacal solution of silver nitrate; test another portion for formic acid, by the addition of mercuric chloride and a solution of sodium acetate. Explain the decomposition.

a. What relation does lactic acid bear to propionic acid?

b. What is sarcolactic acid? How does it differ from the lactic acid obtained from sour milk?

c. How is the theory of the asymmetric carbon atom employed in explaining the isomerism of the lactic acids?

83. β -Hydroxybutyric Acid.

a. To a dilute solution of β -hydroxybutyric acid, add a few drops of a 5 per cent. solution of ferrous sulphate and several drops of hydrogen peroxide. Cf. § 7, Acetoacetic acid.

b. What significance does this reaction have in connection with the chemistry of urine?

c. What would be found by heating β -hydroxybutyric acid with concentrated sulphuric acid?

d. What are some of the chief differences observed in the chemical behavior of α -, β -, and γ -hydroxyacids?

84. Tartaric Acid. How is tartaric acid prepared commercially? How can it be prepared synthetically?

a. **Salts. Calcium Tartrate.** Make a solution of sodium potassium tartrate. To a cubic centimeter of this solution, add a strong solution of calcium chloride. Collect the white precipitate upon a filter-paper, and wash it thoroughly. Place a little of it in a test-tube, and add a strong solution of sodium hydroxide to it. Prepare the sodium hydroxide from a piece of

solid hydroxide which has been washed once or twice to remove the superficial layer of sodium carbonate. Heat the clear alkaline solution of calcium tartrate; a precipitate will form. If the sodium hydroxide solution of calcium tartrate is not clear, filter it, and then heat it. This is an important reaction in the qualitative test for tartaric acid. (?)

b. Reduction of the Silver Salt. Place a very small amount of calcium tartrate in a test-tube. Add to it a few drops of an ammoniacal solution of silver nitrate, and warm the solution gently for several minutes. What does this experiment show concerning tartaric acid? No equation can be written.

c. Complex Copper Tartrates. To a solution of tartaric acid, add several drops of a solution of copper sulphate and make the mixture alkaline by adding sodium hydroxide. What is Fehling's solution? Repeat the experiment, but in place of copper sulphate, use first ferric chloride, then aluminum sulphate. Will sodium hydroxide alone cause precipitates when it is added to pure solutions of these salts? How do you explain these reactions? [R].

85. Tartar Emetic. Dissolve 5 g. of potassium hydrogen tartrate in 50 c.c. of water. Add 4 g. of antimonious oxide to this solution, and boil the mixture. Filter the solution and allow it to evaporate until crystals form.

86. Diacetyl Derivative of Tartaric Ethyl Ester. Mix 6 g. of acetic anhydride with 4 g. of the diethyl ester of tartaric acid, and add to it 30-40 c.c. of a 10 per cent. solution of sodium hydroxide. Mix these substances intimately by thoroughly shaking them. When the odor of acetic anhydride has entirely disappeared and a solid has formed, separate the acetyl derivative by filtration. Wash it with water, and dissolve it in the least possible amount of boiling alcohol. Add water to the hot alcohol solution, until it begins to show a slight turbidity; then allow the acetyl compound to crystallize. Determine the melting-point of the acetyl derivative. It should melt at 67°.

Ketone Acids.

87. Acetoacetic Ethyl Ester. Tautomerism.

a. Action of Ferric Salts. Add a drop of a dilute solution of ferric chloride to an alcoholic solution of acetoacetic ethyl ester. Cf. § 63, Acetylacetone; § 127, *d*, Phenol.

b. Copper Salt. Shake an ether solution of the ester with an

ammoniacal solution of copper sulphate. Collect the green copper salt and recrystallize it from alcohol. Cf. § 63, Acetylacetone.

c. How is the sodium salt of acetoacetic ethyl ester prepared? What views are held concerning the constitutional formulæ of acetoacetic ethyl ester and its salts? What is meant by the phrase "enol form"? What is the meaning of the term tautomerism?

d. How can acetoacetic acid be made from β -hydroxybutyric acid? What are the products of decomposition when a solution of acetoacetic acid is warmed? What significance do these facts have in connection with the chemistry of urine?

e. How can acetoacetic acid be obtained from its ester? Describe the reactions involved in the "ketonic splitting" and "acid splitting" of alkyl derivatives of acetoacetic ethyl ester.

CHAPTER XVI.

CARBOHYDRATES.

88. Test for Carbohydrates (Molisch's Test modified by Mulliken). Treat a very small crystal of cane-sugar (.05 g.) with 2 drops of a 10 per cent. solution of α -naphthol in chloroform. Down the side of the inclined tube containing this mixture, pour 2 c.c. of concentrated sulphuric acid so that it may form a distinct lower layer. If a carbohydrate is present, a purple-red zone will form in the course of a few seconds. After one or two minutes, add 5 c.c. of water. A purple precipitate will result. Try the same test, but in place of cane-sugar use a small piece of starch; of gum arabic; of filter-paper; of linen; of d-glucose. No equations need be written.

Reactions with Fehling's Solution.

89. Monosaccharides.

a. To six drops of a 10 per cent. solution of d-glucose, add ten drops of Fehling's solution and 3 c.c. of water. Boil the solution, and continue to add the d-glucose solution until the blue color is entirely discharged.

Note 8.—For the preparation of Fehling's solution see § 26, *b*, Acetaldehyde. Fehling's solution is usually prepared of such a strength that each cubic centimeter will oxidize 0.005 g. of glucose. If 20 c.c. of a solution of d-glucose were needed to remove the blue color in 10 c.c. of Fehling's solution, how much d-glucose would there be in 1 c.c. of the sugar solution?

b. In a similar way, try the action of Fehling's solution upon solutions of l-arabinose; of l-xylose; of d-mannose; and of d-galactose. If no precipitate separates at once at room temperature, boil each mixture for two minutes.

c. Try the action of Fehling's solution upon a solution of levulose (fruit-sugar). How do solutions of grape-sugar (d-glucose) and of levulose (fruit-sugar) differ in their behavior towards polarized light? Why is levulose known as d-fructose?

90. Disaccharides.

a. Test a solution of cane-sugar (sucrose, saccharose) with Fehling's solution. If necessary, apply heat for two minutes. Result? Add 0.5 c.c. of concentrated hydrochloric acid to a solution of 5 g. of cane-sugar in 50 c.c. of water. Heat this solution on a water-bath for one hour; prevent evaporation as much as possible. Neutralize 1 c.c. with sodium carbonate and test it with Fehling's solution. How do you explain the results? What is invert-sugar? Why is it given this name? Keep the larger portion of the hydrolyzed cane-sugar solution to use in experiment 50.

b. Treat solutions of maltose (malt-sugar) and of lactose (milk-sugar) with Fehling's solution. Result? What important conclusions concerning the constitutional formula of the three disaccharides used above have been drawn from these experimental differences?

91. Polysaccharides.

a. Starch Solution. Heat 200 c.c. of water to the boiling-point and remove the flame. Mix 1 g. of starch with a little cold water, and stir it into the hot water. Test a portion of this solution with Fehling's reagent. Is there any reduction? Boil the mixture one minute. Does this cause any precipitation of cuprous oxide?

b. Hydrolysis of Starch. After mixing some of the starch paste with about one-tenth its volume of concentrated hydrochloric acid, put it in a flask connected with a reflux-condenser, and heat the flask for one hour on a water-bath. Neutralize the acid with sodium carbonate, and test the solution with Fehling's reagent. How could this process be employed to estimate starch quantitatively?

c. With Fehling's reagent, test a solution of gum arabic; of dextrin; of glycogen; and a piece of moistened cellulose. Record your observations.

d. Hydrolysis of Cellulose. Dissolve pieces of cellulose (filter-paper) in cold concentrated sulphuric acid by triturating them in a mortar until solution results. Add the acid drop by drop. Pour the solution into water, and boil the acid solution for half an hour. Neutralize the solution with sodium carbonate and test it for hexoses. Does it reduce Fehling's solution?





92. Starch Iodide.

To some cold starch solution prepared under "Polysaccharides, *a*," add a drop of a very dilute solution of iodine in water containing potassium iodide. Heat the blue solution; then cool it. Try this same test, but in place of starch, use a solution of glucose; of cane-sugar; of dextrin; of gum arabic; and of glycogen.

93. Phenyl Glucosazone. To the remainder of the solution of hydrolyzed cane-sugar (invert-sugar), prepared under "Disaccharides, *a*," add 8 g. of sodium acetate and 5 g. of phenylhydrazine. Warm this mixture upon a water-bath for 2 hours. Collect the yellow precipitate upon a Büchner funnel, wash it with a little cold acetone, and recrystallize it from the smallest possible amount of boiling 80 per cent. alcohol. Collect the precipitate, dry it upon a piece of porous plate, and determine its melting-point. The recorded melting-point is 205°.

a. What products are found by the hydrolysis of cane-sugar?

b. How do you explain the fact that only one osazone is found in the experiment above? What significance does this have in the choice of configurations for the hexose sugars?

CHAPTER XVII.

AMINO ACIDS.

94. Glycocoll, Glycine, Aminoacetic acid.

Pour 50 c.c. of a 40 per cent. formalin solution into a 200-c.c. flask and add 18 g. of ammonium*chloride. Cool this mixture in ice water. Very slowly, and with frequent shaking of the mixture, add a cold solution of 22 g. of 98 per cent. potassium cyanide in 30 c.c. of water. This process should require about 3 hours. During the last hour and a half, drop in also 13 c.c. of glacial acetic acid.

Methylene-aminoacetonitrile is formed as a solid, and should be collected upon a filter and dried upon a porous plate. The yield will be about 60 per cent. of the theoretical amount.

Cover these crystals with 20 c.c. of cold alcohol previously saturated with hydrochloric acid, and, after an hour, add 100 c.c. of water. Remove the alcohol by distillation, and evaporate the residue to dryness. Recrystallize the product from dilute alcohol. The yield, calculated upon the basis of the methylene-aminoacetonitrile, should be about 80 per cent.

a. The Copper Salt. Mix a solution of the glycine salt with some freshly precipitated copper oxide, and evaporate it until the copper salt commences to crystallize.

b. Glycine combines with acids, as well as with bases, to form salts. What name is applied to inorganic compounds which function both as bases and as acids; e.g., aluminium hydroxide, zinc hydroxide, lead hydroxide? Taking this property of the amino acids into consideration, what constitutional formula has been proposed for glycocoll itself?

c. What are leucine, alanine, asparagine? What are polypeptides and how are they obtained from amino acids? What relation are they supposed to bear to the proteins? What evidence is there in support of this view?

CHAPTER XVIII.

COLLOIDS.

95. I. Suspension Colloids (Suspensoids; Hydrophobic or Lyophobic Colloids).

a. Colloidal Ferric Hydroxide. Examine the colloidal solution of ferric hydroxide which has been given you. Does the solution appear to be homogeneous?

Note 9.—This solution may be prepared by adding ammonium hydroxide to a fairly dilute solution of ferric chloride until the solution of the ferric salt is just neutralized. Place the solution in a dialyzer, and dialyze it against distilled water for some ten days, until the dissolved salts are eliminated.

Do you notice any appreciable change in homogeneity when some of the colloidal solution is diluted with large or small quantities of water? Examine a drop of the colloidal solution under an ultramicroscope or a dark ground microscope. What do you observe?

b. Influence of the Electric Current. Pour some of the colloidal solution of ferric hydroxide into a small U-tube having a rather long connecting arm of small diameter; insert platinum electrodes into the arms of the U-tube, and attach the terminals of the electrodes with several cells connected in series. When a current is passed, what happens immediately? after several minutes? after an hour? after several hours? What do you conclude from this behavior?

c. Precipitation of the Colloid. Effect of Salt Concentration. For the following experiments, it will be necessary to have one or two 5-c.c. pipettes graduated to 0.1 c.c., and a 25-c.c. graduated cylinder or flask. The salt solutions used here and under *d* are all molar.* Starting with a M/10 solution of sodium chloride, prepare 10 c.c. of solutions of approximately the following

* In all of the experiments which follow, N is used to designate equivalent normal solutions; and M, in all cases, to signify molar solutions.

concentrations:— $1/20$; $1/50$; $1/100$; $1/200$; $1/300$ M. Place these solutions in labeled test-tubes arranged in the order of increasing concentration, together with a tube containing 10 c.c. of distilled water for comparison. Drop 0.5 c.c. of the colloidal solution of ferric hydroxide into each tube. In the course of a few minutes, do you observe any change in the appearance of the tubes? Keep these tubes for experiments described later under *e*.

d. Comparison of Precipitates Produced by Various Anions and Cations. With concentrations the same as those used in *c*, prepare a similar series of five tubes with each of the following salt solutions:—M/10 sodium bromide; M/10 sodium iodide; M/10 sodium phosphate (Na_2HPO_4); M/10 sodium sulphate. Add to each solution 0.5 c.c. of colloidal ferric hydroxide solution.

In a similar way, investigate solutions made by diluting a M/10 solution of sodium chloride; a M/10 solution of calcium chloride; a M/10 solution of barium chloride; a M/10 solution of aluminium chloride. When solutions of the different salts of the same concentrations (e.g., M/100) are compared, do you notice any difference in the precipitating effect produced by anions and by cations of different positive and negative values?

e. Heat Effect. Heat some of the tubes in which no precipitates formed. Do not boil the solutions. Does this cause precipitates to form? Reserve other solutions in which no precipitates were produced, and examine them the next day. Have precipitates formed in any of these tubes? What do you conclude regarding the time element in the precipitation of colloids?

f. Colloidal Metals and Sulphides. If practical, these experiments may be tried with a colloidal solution of silver; of platinum; of one of the metallic sulphides, e.g., arsenious sulphide.

96. II. Emulsion Colloids (Emulsoids; Hydrophilic or Lyophilic Colloids).

a. Swelling and "Solution" of Emulsoids. Examine samples of the following solids:—Egg albumin, gelatine, fibrin, gluten, casein, and starch. Drop a small amount of each of these solids into separate test-tubes, and pour a little water upon each sample. Notice that after a time some of the samples swell.

Now, warm them all, at first slightly, and then until the

water boils. Observe that with this treatment others swell, while some apparently go into solution; and that these liquids are then miscible in any proportion with water to give solutions apparently clear.

b. Homogeneity. Examine drops of these solutions under an ultramicroscope. What differences do you notice when you compare the results obtained here with the results obtained with the colloidal solution of ferric hydroxide?

c. Effects of Salt. With a solution of egg albumin, prepared by filtering a solution made by treating white of egg with some ten times its volume of water, repeat some of the experiments with the various salt solutions described above under ferric hydroxide. What results have you obtained? How do they differ from the results obtained with the ferric hydroxide solution?

d. Nature of Certain Albumin Tests. To the solution of egg albumin, add a concentrated (saturated) solution of magnesium sulphate, or of sodium sulphate. How does a solution of ferric chloride, or of dilute acetic acid and potassium ferrocyanide, affect the albumin solution? What is the action of concentrated nitric acid upon it? When these changes are considered, what would you say concerning the nature of some of the ordinary tests for albumin?

e. Swelling of Fibrin Produced by Acid. Choose five test-tubes of uniform diameter, and place in them respectively 20 c.c. of N/250, N/230, N/220, N/210, N/200 hydrochloric acid. To this series, add another tube containing 20 c.c. of distilled water. In each tube place 0.2 g. of finely powdered blood-fibrin, carefully weighed. Shake the tubes occasionally, and inspect them at intervals during a period of 24–48 hours. What changes take place in the appearance of the fibrin? Do the acids of different concentrations affect fibrin in the same way? Is there any relation between swelling and concentration of acid?

f. Swelling of Fibrin Produced by Alkali. Prepare a similar series of tubes containing solutions of sodium hydroxide, or of potassium hydroxide, equivalent in concentration to the acid solutions previously employed. Add to each tube 0.2 g. of fibrin as before. How does the swelling in alkaline solution compare with that observed in acid solution of equivalent concentration, or in distilled water?

g. Influence of Salts upon Swelling Induced by Acids and by Alkalies. Into each of five test-tubes, pour 20 c.c. of N/200 hydrochloric acid; add to these tubes respectively 1, 2, 3, 4, and 5 c.c. of a molar solution of sodium chloride, and enough distilled water to make the total volume 25 c.c. For comparison, prepare two other tubes, one containing 20 c.c. of N/200 hydrochloric acid diluted to 25 c.c.; and the other, 25 c.c. of distilled water. Into each of the seven tubes put 0.2 g. of blood-fibrin carefully weighed. When the tubes have stood for some time, what conclusions do you draw concerning the effect of sodium chloride upon the swelling of fibrin in acid solution?

h. Influence of Anions and Cations upon Swelling. Prepare two more series of tubes containing 20 c.c. of N/100 hydrochloric acid as before under *g*. Here, however, instead of adding different concentrations of the same salt, use the same concentrations of different salts, first with dissimilar anions, and then with dissimilar cations.

To five of the tubes containing acid, add respectively the same volume of molar solutions of sodium chloride, sodium bromide, sodium sulphate, sodium iodide, sodium phosphate. Arrange these tubes beside the comparison tubes containing pure acid and distilled water. To each of the seven tubes add 0.2 gram of blood-fibrin.

Prepare a second series of seven tubes, and to five of the tubes containing acid, add the same volume of molar solutions of sodium chloride, calcium chloride, barium chloride, magnesium chloride and aluminium chloride. To each of the tubes including the comparison tubes of pure acid and water, add 0.2 gram of fibrin.

Record and compare your results. What are saline cathartics? What are saline diuretics? How do they affect colloids?

i. Non-Electrolytes and Swelling. Perform a series of experiments with fibrin and N/200 hydrochloric acid; but use osmotically equivalent solutions of ethyl alcohol or methyl alcohol, of glycerol, of urea, in place of the electrolytes employed above. Solutions of the non-electrolytes which have twice the molar concentration of the solutions of electrolytes found active above will be accurate enough. Since the dissociation of the salts in molar solution is less than 90 per cent., the use of double molar solutions would favor the non-electrolytes provided the effect is an osmotic one. What are the results?

j. **The Swelling of Dried Gelatine Plates. Absorption Curves.** After carefully weighing plates of dried gelatine, drop one of them into a dish containing 100 c.c. of N/20 hydrochloric acid, and another into a dish containing 100 c.c. of

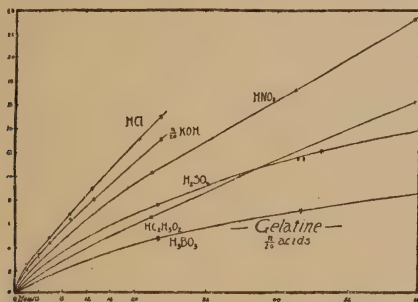


Fig. 18.

N/20 sodium hydroxide. Place one more of these weighed plates in 100 c.c. of distilled water. From time to time, weigh the plates and record the weights. This process should extend over a period of 2-3 days. Plot absorption curves with values calculated in percentage of change based upon the original weights of the dried plates as ordinates, and the times as abscissæ.

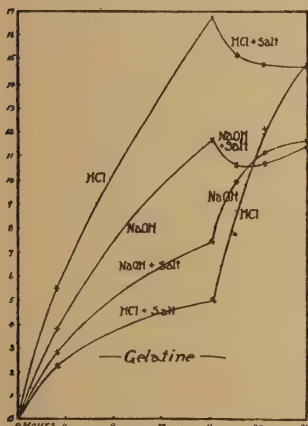


Fig. 19.

The following curves taken from Dr. Martin H. Fischer's work "Œdema" will serve to illustrate the method of plotting such curves. Fig. 18 illustrates the effect of certain acids and alkalis upon gelatine. Fig. 19 illustrates the effect of salts in modifying the swelling of gelatine produced by acids and by alkalis.

Note 10. — The Making of Gelatine Plates. Dissolve one part of the best commercial gelatine (Ne Plus Ultra Gelatine of the

Deutsche Gelatine Fabriken serves the purpose well) in 4 parts of water at a temperature of about 45° . Pour this solution into shallow pans. Allow the gelatine to harden in an ice-chest. With the aid of a sharp knife and a ruler, cut the gelatine into plates of uniform size (2.5 cm. square). Allow the squares to dry upon glass plates in a warm place (30° – 40°). This operation will require from 6–10 days. The plates may conveniently be made of such a size that, when dry, they measure about $18 \times 18 \times 2.5$ mm. They will weigh about 0.8 g. Uniform material is essential, if comparisons are to be made from which valid conclusions may be drawn.

PART II.

AROMATIC COMPOUNDS.

DIVISION 1. CARBOCYCLIC COMPOUNDS.

DIVISION 2. HETEROCYCLIC COMPOUNDS.

CHAPTER XIX.

BENZENE HYDROCARBONS.

97. Benzene.

a. Treat 2 c.c. of benzene with a few drops of a solution of bromine in carbon tetrachloride. What do you observe? Compare this behavior with that observed in the case of amylene. (Cf. § 6.)

b. Shake 2 c.c. of benzene with a dilute solution of potassium permanganate made slightly alkaline by means of sodium carbonate (von Baeyer's reagent). Compare this case with the reaction of ethylene and olefine hydrocarbons toward the same reagents.

c. Add a few drops of bromine to 10 c.c. of benzene, and pour equal portions of this solution into each of two dry test-tubes. To one tube, add some iron filings. What differences do you observe in the velocity of the action in the two tubes, as shown by the evolution of hydrogen bromide?

Is the product formed by the action of one equivalent of bromine upon benzene to be considered as a substitution product, or as an addition product? (?)

d. What is Kekulé's constitutional formula for benzene? In these reactions, does benzene seem to show the behavior which is so typical of an unsaturated hydrocarbon of the aliphatic series?

98. Benzene Sulphonic Acid.

Pour 3 c.c. of benzene and 10 c.c. of concentrated sulphuric acid into a large test-tube; close the tube with a stopper through which a long glass tube, or air-condenser, passes. Shake the tube, and heat it gently until the benzene, which at first floats upon the surface of the acid, has entirely dissolved. Pour a little of this solution into a beaker of water. Does benzene separate when the solution has cooled? Pour the remainder of the solution into about four times its volume of a saturated solution of sodium chloride. Crystals of the sodium salt of ben-

zene sulphonic acid will be precipitated. Collect these crystals on a Büchner funnel; wash them with a little cold water, and dry them. Preserve this salt for a later experiment. (See § 127, *c*, Phenol.)

a. Shake several drops of toluene with one or two cubic centimeters of fuming sulphuric acid, and pour the homogeneous solution into water. Try the same experiment with petroleum ether (benzine). What difference do you observe? Is this a distinctive criterion by which one may judge of the chemical nature of a hydrocarbon; or do the two classes of hydrocarbons, represented by benzene and petroleum ether respectively, respond to the action of concentrated sulphuric acid in a similar manner, but with great disparity in velocity?



CHAPTER XX.

NITROBENZENE AND SOME OF ITS REDUCTION PRODUCTS.

99. Nitrobenzene. Put into a flask 35 c.c. of ordinary concentrated nitric acid (sp. gr. 1.41), and add to it carefully 40 c.c. of concentrated sulphuric acid. Cool the mixture under the water-tap, and add 25 g. of benzene in five or six portions, and with constant shaking of the mixture. The introduction of the benzene should take about half an hour. Then warm the flask at a temperature of 60° on a water-bath for half an hour, and shake it from time to time. The nitrobenzene should float upon the mixture.

Now pour a drop of the contents of the flask into water, and note whether the oil sinks or floats. If the oil is practically

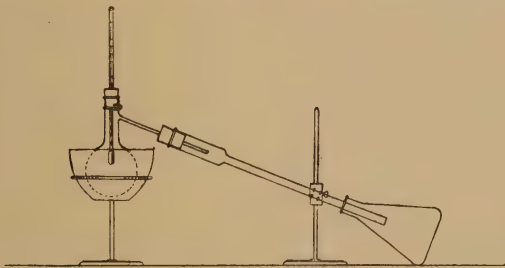


Fig. 20.

free from benzene, it will sink. If the nitration of the benzene has been successful, pour the product into a flask containing about 500 c.c. of water. Shake the mixture thoroughly, cool it, and separate the lower layer of nitrobenzene by means of a separatory-funnel.

Wash the nitrobenzene with water, and dry it thoroughly with fused calcium chloride. Then distill it, using a condenser without a water-jacket. The first cubic centimeter or two will be chiefly benzene and a little water. This should be collected

separately, and should not be allowed to run through the clean condenser-tube. When these impurities have volatilized, the temperature will rise rapidly to the boiling-point of nitrobenzene. At this point, connect the distilling-flask with the condenser-tube, and distill the liquid until the residue in the flask becomes thick and dark brown in color. What is the observed boiling-point?

a. Is this a general method for preparing aromatic nitro-compounds? Can any of the aliphatic nitro-compounds be made in a similar way? What commercial value does this reaction have? What nitrating agents are commonly employed in technical work?

100. Meta-dinitrobenzene. Mix 3 drops of benzene with 1 c.c. of concentrated nitric acid (sp. gr. 1.4) and 1 c.c. of concentrated sulphuric acid (sp. gr. 1.84). Boil the mixture gently for one-half minute. Pour the product into 10 c.c. of water, collect the precipitate upon a small filter, and wash it until the washings are colorless. Dissolve the crystals in 8 c.c. of boiling dilute alcohol (equal parts of water and alcohol). Set the tube aside, and allow the solution to cool; long needles of meta-dinitrobenzene will form. Collect these crystals upon a filter, wash them with 5 c.c. of dilute alcohol (1 : 1); dry them, and determine their melting-point. The recorded melting-point is 90°. Small quantities of benzene may be identified by this reaction.

101. Azoxybenzene. Dissolve 15 g. of nitrobenzene in 125 c.c. of methyl alcohol, and add to it 20 g. of powdered sodium hydroxide. Heat the mixture for two hours upon an actively boiling water-bath. Remove most of the methyl alcohol by distillation, and pour the dark residue into ice water. Azoxybenzene will separate as an oil, which, however, will soon solidify. Collect the solid upon a Büchner funnel, and wash it. After shaking this residue with some warm dilute hydrochloric acid for a few minutes, cool it until it solidifies once more; collect it upon a filter and wash it. To purify this crude azoxybenzene still further, recrystallize it from warm alcohol (90 per cent.). The melting-point is 36°.

102. Azobenzene.* Pour 125 c.c. of methyl alcohol into a flask (about 1-liter) and add 12.5 g. of nitrobenzene. Connect

* Suggested by Dr. H. S. Fry, University of Cincinnati.



the flask with a reflux-condenser, and add 7.4 g. of powdered magnesium. If the action does not commence at once, a crystal of iodine may start it. The vigorous action which follows should be controlled by submerging the flask in cold water. The reaction requires ten or fifteen minutes for completion; the end is reached when the odor of nitrobenzene has disappeared.

After removing most of the methyl alcohol by distillation, transfer the residue to an evaporating-dish, and heat it upon a steam bath until it becomes dry. Pulverize the residue and extract the azobenzene with ether, preferably in a Soxhlet apparatus. When the ether is removed, recrystallize the azobenzene from methyl alcohol. The melting-point is 68° . The yield should be about 95 per cent. of the calculated amount.

a. Is azobenzene a "dye"? Why is it called a chromogen? What is a chromophor group? an auxochrome group?

103. Hydrazobenzene. Dissolve the azobenzene in boiling alcohol, and add zinc dust to it in small portions until the red color is entirely discharged. Filter the hot solution rapidly. To the filtrate, add hot water which contains a little sulphurous acid (?) until the solution becomes slightly turbid; then set it aside, and allow the hydrazobenzene to separate as the solution cools. Collect the precipitate upon a filter, wash it with water containing sulphurous acid, and dry it. The melting-point is 126° .

a. How can hydrazobenzene be changed to azobenzene? to aniline?

b. Does hydrazobenzene reduce Fehling's solution?

104. Benzidine Salts. "Benzidine Rearrangement." The hydrazobenzene obtained above should be treated with one and a half times its weight of concentrated hydrochloric acid and twice its weight of water, and then boiled gently for a few minutes. When the acid solution is cooled, benzidine hydrochloride

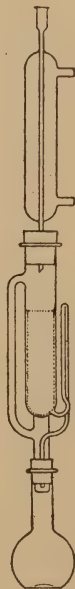


Fig. 21. Soxhlet Extractor.

will separate. Collect the crystals upon a filter and purify them by recrystallization from water.

Add a few drops of sulphuric acid to the filtrate. Benzidine sulphate is soluble with difficulty, and will separate.

a. How could you prepare benzidine from its salts? How is benzidine employed in making dyes?

b. Does benzidine hydrochloride reduce Fehling's solution?

105. Aniline. Into a 500-c.c. flask put 15 g. of nitrobenzene and 27 g. of granulated tin, and add, in small portions, 100–150 c.c. of strong hydrochloric acid. Shake the flask frequently. The mixture will become so warm that the reaction must be controlled by occasionally cooling the flask. The reaction will be complete when the odor of nitrobenzene has almost disappeared. During the course of the experiment, a white double salt of tin chloride and aniline chloride will usually separate. At the close of the operation, add water enough to dissolve this salt; then pour off the solution, leaving the excess of tin in the flask. To remove any unchanged nitrobenzene, cool the solution thoroughly, place it in a separatory-funnel, and extract it two or three times with small portions of ether. This ether extract should be thrown away. What does it contain, and why is the extraction desirable?

To the acid solution separated from the ether, add solid caustic soda until the stannic acid and stannous hydroxide which form at first are almost redissolved. Care! If the solution grows very warm, cool it immediately before you add any more sodium hydroxide. Most of the aniline will separate as an oil. It will be safer, however, to add the sodium hydroxide until the solution reacts strongly alkaline towards litmus. In some cases, the oil may not separate, but may remain completely dissolved.

Arrange an apparatus like the one described under chloroform, and distill the aniline in a current of steam until no more oil drops pass over. Extract the distillate with ether, and dry the ether solution with solid sodium-hydroxide; then filter it, distill the ether from a water-bath, and fractionate the aniline in a small distilling-bulb. The condenser needs no jacket. What yield have you obtained?

a. What relation does aniline bear to benzene? to ammonia? to methylamine?

b. Shake a drop of pure aniline with a few cubic centimeters of pure distilled water (ammonia free), and test the clear solution with a piece of neutral litmus paper. What is the reaction?

c. Add some of this solution to a solution of ferric chloride; of zinc chloride; of aluminium chloride. In view of the reaction shown in *b*, how do you account for the observations which you have made with these salt solutions?

d. Dissolve a drop of aniline in the least possible amount of dilute hydrochloric acid. Why does aniline dissolve easily in acids, while it is soluble with difficulty in water? Add a few drops of this acid solution to a solution of hydrochlorplatinic acid. What is the formula of the compound which is precipitated? [R]. Does ammonium chloride react in a similar way with hydrochlorplatinic acid? (Cf. § 52, Methylammonium Chloride.)

106. Phenylammonium Chloride, Aniline Hydrochloride.

Pour 15 g. of freshly distilled aniline into a mortar, and add to it a little more than one equivalent of pure hydrochloric acid in the form of concentrated acid (sp. gr. 1.18). When the two substances have been thoroughly mixed by rubbing them together with a pestle, cool the product and collect the salt upon a Büchner funnel. Drain the salt thoroughly upon a Büchner funnel by applying suction with a filter-pump, and dry the solid in a beaker upon a water-bath. This salt will be needed for later experiments. Cf. §§ 109, 112.

107. Hydrolysis of Aromatic Amine Salts.

a. Test a solution of pure aniline hydrochloride in water with Congo red paper, then with neutral litmus paper. Explain your results. Are any oil drops of aniline visible in this solution?

b. Dissolve about 0.5 g. of para-nitraniline in the smallest possible amount of boiling concentrated hydrochloric acid. Filter the hot solution and cool it under the tap; the hydrochloride of para-nitraniline will be precipitated. Collect the crystals upon a filter and dry them thoroughly to remove all traces of free hydrogen chloride. Transfer them to a watch-crystal, and moisten them with a few drops of water. How do you explain the change of color? With neutral litmus paper, test the liquid which surrounds the yellow precipitate. Explain your observations.

c. Dissolve a few crystals of diphenylamine in a little alcohol, and pour the solution into water. Add concentrated hydrochloric acid, a drop at a time, until the diphenylamine dissolves. If water is added to the clear solution, diphenylamine will be precipitated. Explain.

d. From the observations which you have just made, what seems to be the influence of nitro groups and of phenyl groups upon the base-forming power of aniline? Is there any generalization covering these cases and others of a similar nature? Cf. Appendices D and E.

108. Acetanilide, Antifebrin. Put 5 g. of aniline and 7 g. glacial acetic acid in a small flask, connect the flask with a reflux-condenser, and heat the flask over a wire gauze. The mixture should boil gently for 4 or 5 hours.

At the end of this time, pour the product into 200 c.c. of cold water. Filter the mixture, wash the crystals with dilute hydrochloric acid, and recrystallize the acetanilide from hot water. If the crystals are colored, add a small amount of animal charcoal to remove the color during the process of recrystallization. Dry some of the crystals and determine the melting-point. Acetanilide is known as antifebrin.

a. Heat some of the crystals with a strong solution of sodium hydroxide. What is formed? Boil a few crystals with dilute sulphuric acid (1 : 1). Notice the odor of the vapor. (?)

b. How does acetanilide differ from aniline acetate? Is aniline acetate formed in this preparation? What would be obtained by heating ammonium acetate?

c. Heat 2 c.c. acetyl chloride with 1 c.c. of aniline, and treat the product with water. Separate the crystals and recrystallize the substance from a little boiling water. Compare the melting-point of these crystals with the melting-point of a sample of acetanilide prepared above.

d. Warm 1 c.c. of acetyl chloride with 1 c.c. of monomethylaniline; then heat 1 c.c. of acetyl chloride with 1 c.c. of dimethylaniline. Pour each product into water. Is there evidence of chemical change in each case? Are the reactions illustrated in c and d typical of primary, secondary, and tertiary amines in general?

CHAPTER XXI.

DIAZONIUM SALTS AND DIAZO COMPOUNDS. AZO-DYES.

Diazonium Compounds.

109. Benzene Diazonium Chloride (Solid). Make a solution of 5 g. of solid aniline hydrochloride in 35 c.c. of absolute alcohol containing a few drops of hydrochloric acid. Cool it until the temperature is about $+5^{\circ}$, and add 6 g. of amyl nitrite. This process is called diazotizing.

The success of the operation may be determined as follows:— To a drop of the solution, placed upon a water-glass, add a drop of a solution of sodium acetate; a yellow precipitate will indicate an excess of the aniline salt and insufficient nitrite. If this should be the case, add a little more nitrite, and apply the test with acetate again. Finally, sodium acetate should give no yellow precipitate; but, even after long standing, a drop of the solution placed on a water-glass must give a blue color with a little starch solution containing potassium iodide. (?)

To promote the separation of the diazonium salt, add a few drops of ether. (?) Collect the precipitate upon a funnel, and wash it with ether. Dry a very small amount of it, and heat it upon a metal spatula. (Explosive!) Dissolve the remainder at once in 50 c.c. of water cooled to $+5^{\circ}$.

110. Benzene from a Diazonium Salt. The diazonium chloride solution prepared in the previous experiment should be poured into a cold solution of sodium hydroxide containing 10 g. of sodium hydroxide dissolved in 30 c.c. of water. Make an alkaline solution containing 20 g. of stannous chloride ($\text{SnCl}_2, 2 \text{H}_2\text{O}$), and add it gradually to the former solution. When the resulting mixture is distilled, benzene and water vapor will pass over. About 4 g. of benzene can be separated from the distillate. This method is frequently employed to convert amino-compounds into hydrocarbons; or, expressed in hypothetical terms, "to eliminate amino groups." Alcohol is sometimes employed as a reducing agent in place of stannous chloride.

Benzene may be identified by its boiling-point, or by conversion into m-dinitrobenzene. (Cf. § 100.)

a. What is Sandmeyer's reaction?

b. By the intermediate formation of diazonium salt, how could aniline be changed into phenol? into iodobenzene? into benzonitrile?

Diazo Compounds.

111. Para-nitrophenyl-antidiazotate. Dissolve 7 g. of p-nitraniline in 25 c.c. of hot dilute hydrochloric acid (1:1); pour this solution upon crushed ice, and add 4 g. of sodium nitrite dissolved in 13 c.c. of water. Some ice should remain at this point. To make sure that sufficient nitrite has been used, apply the test with sodium acetate described in § 109.

When enough nitrite has been added, stir the turbid solution until it becomes practically clear, and filter it rapidly through a funnel containing a loose plug of cotton. Test the filtrate to make sure that sufficient nitrite has been used. Dissolve about 20 g. of sodium hydroxide in 200 c.c. of water; and, with the temperature of this solution at 60°, pour the diazonium solution rapidly into it. Golden-yellow crystals of sodium p-nitrophenyl-antidiazotate will separate abundantly when the mixture is thoroughly cooled.

Collect the crystals upon a Büchner funnel, and wash them carefully with a little ice-cold water. Dissolve them in 90 per cent. alcohol at a temperature not exceeding 60°. Filter the solution, and allow it to stand until the salt crystallizes. The yield will be about 6 g. The corresponding syndiazotate has not been prepared. (Schraube and Schmidt, Ber. **27**, 518.)

a. Make a dilute water solution (30 c.c.) of the sodium antidiazotate, and pour 5 c.c. of it into an alkaline solution of α -naphthol; of β -naphthol.

b. Acidify 5 c.c. of the solution of the antidiazotate by adding dilute hydrochloric acid until the solution reacts distinctly acid. What does this solution contain? Pour some of this acidulated solution into an alkaline solution of α -naphthol; of β -naphthol. The alkali must be in excess.

c. Acidify 5 c.c. of the original solution of the antidiazotate, but make it distinctly alkaline before you pour it into an alkaline solution of α -naphthol; of β -naphthol.

d. What are syndiazotates? What rôle do they play in the formation of azo-dyes? How are they changed into anti-diazotates? How are antidiazotates changed into diazonium salts? into syndiazotates? In view of these relations, explain the observations which you have made in performing experiments *a*, *b*, and *c* above.

Azo Dyes.

112. Benzene Diazonium Chloride Solution. To a mixture of 21.5 c.c. ($2\frac{1}{2}$ mols) of concentrated hydrochloric acid (sp. gr. 1.18) and 20 c.c. of water, add 10 g. of aniline (1 mol). Put into this solution enough crushed ice to keep the temperature of the solution below 10° during the following operation. Dissolve 7.7 g. of sodium nitrite in 20 c.c. of water, and add it slowly to the solution of the aniline salt. At the end of this process, called "diazotizing," there should be some ice left. A sample of this product placed upon a watch-crystal and treated with an excess of a solution of sodium acetate, should give no yellow color or precipitate. The appearance of a yellow precipitate or color indicates insufficient nitrite; should this occur, add a little more nitrite solution, and test the diazo solution again. When enough nitrite is present, a drop of the diazonium chloride solution, when brought in contact with starch and potassium iodide, should show the starch-iodide test, if not immediately at least after a short time. In the preparation just described, what is the yellow precipitate formed by the addition of sodium acetate?

113. "Coupling" of Diazo Compounds with Amines and with Phenols.

a. With amines. To a water solution of dimethylaniline hydrochloride, add a little of the diazonium chloride solution and a slight excess of sodium acetate solution. Pour some of the diazonium chloride into an alcoholic solution of α -naphthylamine and of β -naphthylamine, and add an excess of sodium acetate. What are the products formed in these reactions?

b. Add some of the diazonium chloride solution, first to a solution of naphthionic acid dissolved in an excess of sodium hydroxide, and then to a solution of naphthionic acid in an excess of sodium acetate.

c. With phenols. Add some of the diazonium chloride solution to solutions of phenol; of resorcinol; of α -naphthol; of

β -naphthol. These substances should be employed first in acetic acid or alcohol solution; second, in acetic acid with an excess of sodium acetate; third, in a dilute solution of sodium hydroxide. Explain the reactions in each case.

114. Diazoaminobenzene. Pour one-half of the diazonium chloride solution prepared in § 113 into a beaker cooled by surrounding it with ice, and add 6 g. of solid aniline hydrochloride. (Cf. § 106.) Make a concentrated solution of sodium acetate containing $2\frac{1}{2}$ mols and add it to the solution made above. After an hour or two, collect the precipitate upon a funnel connected with a filter-flask and pump; drain it thoroughly and wash it with water. When it has been dried upon a porous plate, recrystallize it from low-boiling ligroïne or gasoline. A flask connected with a reflux-condenser should be employed in this process. Diazoaminobenzene should form golden-yellow crystals, which should melt at 98° . The yield should be about 70 per cent. of the amount calculated.

a. Dissolve a small amount of diazoaminobenzene in alcohol, and add to it an alcoholic solution of silver nitrate.

b. Treat a little of the diazo-compound with dilute hydrochloric acid. Treat a second portion with hot concentrated hydrochloric acid. Explain these changes.

115. Aminoazobenzene. Mix 1 g. of diazoaminobenzene with a little aniline hydrochloride (0.5 g.), and add to it about twice its volume of aniline. Heat this mixture at a temperature of about 40° – 50° for 15–30 minutes. Pour this reaction product into an excess of very dilute acetic acid. Collect the separated solid and wash it with water. Boil the precipitate with 200 c.c. of water, and add concentrated hydrochloric acid cautiously until a sample of the deep-red liquid when cooled will deposit steel-blue needles. Filter the hot solution, and allow it to stand and cool until the crystals of the hydrochloride of aminoazobenzene have separated.

Aminoazobenzene itself may be made from the salt suspended in twice its volume of alcohol, by the action of concentrated ammonium hydroxide, added drop by drop, until the salt is dissolved and the color of the solution becomes brown. By careful treatment with water, aminoazobenzene will separate in yellow crystals. It may be recrystallized from dilute alcohol.

a. Immerse a piece of white woolen yarn in a hot solution of the hydrochloride of aminoazobenzene. After 10 minutes remove the yarn and wash it. Is it dyed? Can the color be removed by washing?

116. Bismarck Brown. (First Azo-dye, 1866.) Make a dilute solution of meta-phenylenediamine, add to it a small crystal of sodium nitrite and a drop of dilute sulphuric acid. What is the nature of the reaction? How is this reaction employed to detect and to estimate very small quantities of nitrites in drinking-water?

117. Helianthin. (Methyl Orange.) Dissolve 4.3 g. of sulphanilic acid in a dilute solution of sodium hydroxide containing 1 g. of the base. Add the calculated amount of sodium nitrite required to diazotize the sulphanilic acid; and, after cooling the mixture, pour into it the calculated amount of hydrochloric acid (1 mol). Dissolve the equivalent amount of dimethylaniline in a little hydrochloric acid and add it to the diazonium solution just prepared. When the mixture is made alkaline by the addition of sodium hydroxide, the azo-salt will separate at once. Collect the precipitate upon a filter and recrystallize it from hot water.

a. To a hot solution of the sodium salt, add dilute acetic acid.

b. To a hot solution of the salt, add an excess of concentrated hydrochloric acid. How do you explain the different results obtained in *a* and *b*? (Cf. Hantzsch, Ber. **41**, 1187 (1908); Stieglitz, J. Am. Chem. Soc. **25**, 112 (1903).)

c. Reduction of Helianthine. Dissolve 3 g. of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 6 c.c. of concentrated hydrochloric acid. Make a hot concentrated solution of helianthine (1 g.), and add the stannous chloride solution to it, until the color is entirely removed. When the mixture is cooled and stirred, sulphanilic acid will separate. What is the other reduction product?

Benzidine Dyes.

118. Benzoblue. (Disazo-dye.) Dissolve 2.3 g. of benzidine in 7 g. of hydrochloric acid (sp. gr. 1.18) and 125 c.c. of water. Diazotize this solution, cooled by ice, by adding 1.7 g. of sodium nitrite dissolved in 10 c.c. of water. Pour the solution into an alkaline solution of 1,8-amino-naphthol 3,6-disulphonic acid

("H acid"). The dye will separate in brilliant needles. This dye will color wool without a mordant.

a. What is Congo red? Trypan blue?

119. Polyazo-dye. Dissolve this benzoblue in slight excess of hydrochloric acid, and add to it the calculated amount of a sodium nitrite (.08 g. of nitrite for 1 g. of benzoblue). A deep greenish-blue diazonium compound will be formed. If this solution is poured into an alkaline solution of resorcinol, a dye will be formed which will color cotton green without a mordant. What is the meaning of the term substantive dye? adjective dye?

CHAPTER XXII.

PHENYLHYDRAZINE. NITROSAMINES. NITROSOPHENOL. DIPHENYLAMINE DYES.

120. Phenylhydrazine by the Reduction of a Diazonium Compound. Dissolve 10 g. of aniline in 100 c.c. of concentrated hydrochloric acid. Cool the solution thoroughly by surrounding it with ice, and diazotize it by adding the calculated amount of sodium nitrite. Pour the solution slowly into a cold solution containing 60 g. of stannous chloride ($\text{SnCl}_2, 2 \text{H}_2\text{O}$) dissolved in concentrated hydrochloric acid. The hydrochloride of phenylhydrazine will be precipitated.

After a short time, collect the crystals and drain them thoroughly. This can be done best by means of a Büchner funnel and a pump. Treat the crystals with a slight excess of a solution of sodium hydroxide, and extract the liberated hydrazine by means of ether. When the ether solution has been dried (12 hours) over solid potassium hydroxide, separate the solid and remove the ether by distillation. Distill the phenylhydrazine *in vacuo*. Cf. Fig. 17. An oil-bath or a metal-bath must be used to get a temperature high enough. At 12 mm., phenylhydrazine will boil when the temperature of the bath lies between 120° – 140° .

a. What is the action of Fehling's solution upon phenylhydrazine?

b. Compare the process of reduction of benzene diazonium chloride in an alkaline solution of stannous chloride, with the process of reduction used above in the preparation of phenylhydrazine.

121. Para-nitrosodimethylaniline and its Hydrochloride. Mix 5 g. of dimethylaniline with 10.5 c.c. of concentrated hydrochloric acid, and add to it some crushed ice (15 g.). Dissolve 3.2 g. of sodium nitrite in 10 c.c. of water, and add this solution gradually to the cold solution of the dimethylaniline salt. The hydrochloride of p-nitrosodimethylaniline will separate. Allow

the mixture to stand twenty minutes; then collect the salt upon a Büchner funnel, wash it with alcohol and ether, and recrystallize it, using 12 parts of dilute hydrochloric acid (1 : 1). It must not be heated above 60° during the process of solution. Its melting-point is 177°.

To prepare the free nitroso-compound, suspend a part of the salt in water, and add a 10 per cent. solution of sodium carbonate until the yellow salt is decomposed. Extract the green nitroso-compound with a small amount of ether. Remove most of the ether by distillation, pour the remaining concentrated solution into an Erlenmeyer flask, and allow the solvent to evaporate until crystals of the nitroso-compound have separated. The melting-point is 77°.

a. Reduce a portion of the nitroso-compound, using a hydrochloric acid solution of stannous chloride as the reducing agent.

b. To another portion of the nitroso-compound, add a few drops of a solution of potassium permanganate. What is precipitated? How could you identify it?

c. Compare the behavior of dimethylaniline, a tertiary aromatic amine, towards nitrous acid, with the behavior of aniline, a primary amine, and methyl aniline, a secondary aromatic amine, towards the same reagent. Have nitroso-derivatives resembling nitroso-dimethylaniline in form been obtained from primary and secondary amines? [R].

Diphenylamine Dyes and Related Dyes.

122. Indoanilines. To a solution of phenol or of resorcinol in sodium hydroxide, add a small amount of nitroso-dimethylaniline. Shake the mixture with zinc dust until the color is removed. Filter the solution, and shake it with air. Explain the changes observed. Substitute α -naphthol for phenol, and repeat the experiment.

123. Indamines. "Toluylene Blue." Mix a water solution of nitroso-dimethylaniline hydrochloride with a small amount of meta-toluylendiamine. To one portion, add sodium hydroxide; to a second portion, add an excess of hydrochloric acid.

124. Thiazine Dye. Methylene Blue. To a solution of p-nitrosodimethylaniline hydrochloride, add a few drops of ammonium sulphide and warm the solution gently. What is formed by the action of the sulphide? After a few seconds, add an excess of dilute hydrochloric acid and a few drops of ferric

chloride. Methylene blue will result. What is the formula of methylene blue? What relation does it bear to the indoanilines?

125. Safranine Dye. Mauve. (First Commercial Aniline Dye; Perkin, 1856.) Heat 1 g. of commercial aniline containing toluidine with a small excess of hydrochloric acid. To the clear solution, add a few cubic centimeters of a dilute solution of potassium dichromate.

126. Para-nitrosophenol, Quinone Monoxime. Heat a solution containing 25 g. of sodium hydroxide solution (sp. gr. 1.25) and 225 c.c. of water in a round-bottomed flask connected with a condenser and a receiver containing dilute hydrochloric acid. The end of the condenser-tube should just touch the surface of the acid in the receiver. To this solution, add small portions of p-nitrosodimethylaniline until 5 g. have been added. After the addition of each portion, close the flask, and allow the nitroso-compound to dissolve before a fresh sample is introduced. When all of the nitroso-compound has been used, boil the mixture until the dark-green color changes to a reddish-yellow tint.

Cool the alkaline product, acidify it with sulphuric acid, and extract it with ether. When the ether has been distilled, nitrosophenol will be left as a brown crystalline solid. Separate it, and dry it. It decomposes with a slight explosion at 120°–130°.

If the hydrochloric acid in the receiver is evaporated on a water-bath, dimethylammonium chloride will be obtained.

a. Liebermann's "Nitroso" Reaction. Dissolve a few crystals of nitrosophenol (quinone monoxime) in an excess of phenol, and warm this mixture with concentrated sulphuric acid. A blue color will appear, which will change to red when the product is poured into water.

CHAPTER XXIII.

PHENOLS AND SOME RELATED COMPOUNDS.

127. Phenol by the Diazo-reaction.

Pour 10 g. of aniline into 300 c.c. of water, and add gradually 8 c.c. of concentrated sulphuric acid. With this solution, cooled to 40° – 50° , mix a solution of sodium nitrite containing the calculated amount necessary to diazotize the aniline salt. Heat this solution for 30 minutes on a water-bath at a temperature varying from 40° – 50° . When a current of steam is passed into this liquid, phenol will distill. Add sodium chloride to the distillate, and extract the phenol by means of ether. Dry the ether extract, and subject the solution to fractional distillation. Phenol boils at 183° .

a. Treat a small amount of phenol with a strong solution of sodium hydroxide. What do you observe? Acidify the alkaline solution. What is the result?

b. Dissolve a drop of phenol in water, and add bromine water to it as long as the bromine is readily absorbed. Collect the precipitate upon a filter, dry it on a piece of porous plate, and determine its melting-point. This compound, 2,4,6-tribromophenol, is frequently used in detecting the presence of and in determining the quantity of phenol.

c. **Phenol from Benzene Sulphonic Acid.** Fuse 1 g. of sodium hydroxide in a small porcelain crucible, and add 0.5 g. of sodium benzene sulphonate. Cf. § 98. Continue the heating for five minutes, but avoid a temperature high enough to cause the fused mass to char. Cool the product and dissolve it in water. After making the solution acid by means of hydrochloric acid, filter it, and notice the odor of the filtrate. (?) Add bromine water in slight excess to the filtrate. Collect the precipitate, wash it, dry it, and determine its melting-point. (Cf. test *b* above.)

d. To a dilute solution of phenol, add a few drops of a dilute solution of ferric chloride.

e. Make dilute solutions of pyrocatechin and of resorcinol, and test each with ferric chloride. To the pyrocatechin solution containing ferric chloride, add some sodium carbonate. This change in color is characteristic of pyrocatechin.

f. Compare the behavior of the phenols with the reactions of acetoacetic ethyl ester and acetylacetone in the presence of ferric chloride. Cf. § 63 and § 87.

128. Anisol, Phenyl Methyl Ether. Dissolve 15 g. of phenol in 50 c.c. of water and 20 c.c. of 10 N. sodium hydroxide. Pour this mixture into a flask (250 c.c.) and add slowly 25 c.c. of dimethyl sulphate (commercial). Dimethyl sulphate is odorless, but extremely poisonous. Be careful not to breathe the vapor. Perform the operation under a hood. The mixture will become so warm that thorough shaking and cooling of it will be necessary to keep the temperature between 40° and 50°, as shown by a thermometer placed in the mixture. At first, the clear liquid will become turbid; and, in the course of a few minutes, a light layer of oil will float upon the surface. The reaction may be considered complete when the product no longer becomes warm spontaneously. (Cf. §75, Methyl Thiocyanate.)

To destroy the excess of dimethyl sulphate, warm the mixture to the boiling-point, and shake it frequently. Finally, cool the liquid, make it slightly alkaline, and extract it with ether. Dry the ether solution with anhydrous potassium carbonate. When the ether has been removed by distillation from a water-bath, distill the ether, and then the anisol. Anisol boils at 155°. The yield will be about 90 per cent. of the theoretical amount.

a. In what sense may anisol be considered as an ester?

129. Phenyl Benzoate. After mixing 0.5 g. of phenol with 5 c.c. water, add to it 0.8 g. of benzoyl chloride and enough sodium hydroxide solution to make the mixture slightly alkaline, even after it has been warmed and shaken. After the odor of benzoyl chloride has disappeared, cool the solution and allow it to stand for a short time. When the ester has solidified, collect it on a filter, wash it, and recrystallize it from alcohol. Dry the crystals, and determine the melting-point (69°).

a. If this substance were boiled with a solution of sodium hydroxide, what would be formed? Try the reaction. Acidify the alkaline solution. What is precipitated?

130. Ortho- and Para-nitrophenol. Dilute 27 c.c. of concentrated nitric acid with 70 c.c. of water and cool the mixture in a stream of water. To this dilute acid, add 20 g. of phenol in several small portions. While the phenol is being added, shake the flask constantly, and keep it cool. Allow the mixture to stand for 12 hours. When the layer which forms has been separated and washed with twice its volume of water, subject it to distillation in a current of steam.

The Ortho Compound. Steam will carry over the ortho-nitrophenol in the form of a yellow oil, which will solidify partially in the condenser-tube. Collect these crystals and dry them on a porous plate; they are practically pure. They may be very successfully recrystallized as follows: — Dissolve them in 5 times their weight of dry ether and add $2\frac{1}{2}$ times their weight of petroleum ether. Pour this solution into an Erlenmeyer flask cover the flask loosely with a cap of filter-paper, and allow it to stand until the substance has crystallized. What is the principle involved in this method?

The Para Compound. The para-nitrophenol, — which is not volatile with steam, — will remain in the flask as a brown tarry mass. In order to purify it, boil it for some time with a dilute (5 per cent.) solution of sodium hydroxide, and filter the dark-colored solution.

Heat the filtrate with animal charcoal, and filter it again. When this alkaline solution has been concentrated to about one-third its original volume, treat it with a strong solution (50 per cent.) of sodium hydroxide. The sodium salt of para-nitrophenol will separate as the solution cools. Collect it upon a filter, dissolve it in the smallest amount of hot water possible, and precipitate it again by means of a concentrated solution of sodium hydroxide. (?)

When the purified salt is suspended in water and treated with dilute sulphuric acid, para-nitrophenol will be formed. To purify it still further, recrystallize it from a small amount of hot water.

a. Treat a few crystals of o-nitrophenol and of p-nitrophenol with a solution of sodium hydroxide. What is formed? Pass carbon dioxide through these solutions. Are the nitrophenols precipitated? Repeat the experiment, using phenol in place of the nitrophenols. Which is the more active acid, o-nitro-





phenol or phenol? Compare the hydrolysis of aniline salts and salts of substituted aniline derivatives with the behavior of these substituted phenols. Cf. Appendices D. and E. Do the nitrophenols decompose carbonates?

b. How is the fact explained that para-nitrophenol and its esters are colorless while its salts are colored? (Hantzsch and Gorke, Ber. **39**, 1073, 3074.)

✓ **131. Picric Acid.** Dissolve 0.1 g. of phenol in 2 c.c. of concentrated sulphuric acid. Pour this solution gradually into a mixture of 2 c.c. of concentrated sulphuric acid and 2 c.c. of concentrated nitric acid. After heating this mixture on a water-bath for 5–10 minutes, pour it into about 70 c.c. of cold water. When the product is cool, collect the precipitate upon a filter, and wash it with a mixture of 2 c.c. of water and 0.5 c.c. of concentrated hydrochloric acid. (?) Recrystallize the picric acid, using for this purpose a boiling mixture of 4 c.c. of water and 1 c.c. of concentrated hydrochloric acid. When the precipitate has separated from the cool solution, collect it, and wash it with dilute hydrochloric acid as before. The melting-point is 122°.

a. Is picric acid a more active acid than phenol? Does it decompose carbonates?

b. How is picric acid employed as an explosive? as a dye?

132. Para-amidophenetole from Phenacetin. Boil 5 g. of commercial phenacetin with 10 c.c. of concentrated hydrochloric acid and 10 c.c. of water. A few pieces of porous plate placed in the flask will prevent "bumping." The hydrolysis will be complete in 20–30 minutes. When the solution has cooled, the odor of acetic acid will be noticeable, and the hydrochloride of para-amidophenetole will separate. Cf. §108, Acetanilid. The hydrochloride melts at 234°.

Para-amidophenetole may be made from this salt as follows: — Dissolve one-half of the salt in water, and add a 10 per cent. solution of sodium hydroxide to it until the solution reacts distinctly alkaline. Separate the oil which forms, and extract the alkaline solution by means of ether. After drying the ether over potassium hydroxide, remove it, and distill the para-amidophenetole. The boiling-point is 142°.

a. Treat a water solution of it with ferric chloride.

133. Dulcin, p-Phenetole urea. Dissolve 2 g. of the hydrochloride of p-amidophenetole in 10 c.c. of water, and mix this

solution with a concentrated solution of 1.2 g. of potassium cyanate. The liquid will become filled with crystals of the urea. Collect the crystals upon a funnel, and recrystallize them from alcohol. Dulcin is about as sweet as cane-sugar. It is *poisonous*.

a. In what respect does this reaction resemble the reaction involved in the preparation of urea from potassium cyanate and ammonium salts?

CHAPTER XXIV.

ALDEHYDES AND KETONES.

Aldehydes.

134. Benzaldehyde.

a. Shake several drops of benzaldehyde with a concentrated solution of sodium hydrogen sulphite. Collect the crystals upon a filter-paper, dry them, and heat them with a solution of sodium carbonate. Cf. §28, Acetone.

b. Mix benzaldehyde with a solution of phenylhydrazine in 50 per cent. acetic acid. What is formed? Cf. § 28, Acetone.

c. Does benzaldehyde reduce an ammoniacal solution of silver nitrate?

d. Rub a small amount of benzaldehyde on a watch-crystal, and allow it to stand exposed to air for some time. What change has taken place?

e. Make a dilute solution of potassium iodide containing starch emulsion (cf. §92, Starch Iodide). Add a drop of benzaldehyde to it. Shake the mixture frequently, and allow it to stand in the sunlight. What are oxidases?

135. Meta-nitrobenzaldehyde. Mix 100 c.c. of concentrated sulphuric acid and 8.5 c.c. of fuming nitric acid. Cool this acid to 0° in a freezing-mixture of ice and salt, and allow 25 g. of commercial benzaldehyde to flow into the acid very slowly, while the mixture is being stirred. During this stage, the temperature should not exceed +5°. Pour this product into a flask, and heat it slowly upon a water-bath until the temperature reaches 40°.

Cool the product, and pour it slowly upon some crushed ice. Collect the m-nitrobenzaldehyde upon a Büchner funnel; dry it, and recrystallize it from a mixture of benzene and ligroïne. Its melting-point is 58°.

a. How do you explain the fact that benzaldehyde is oxidized on exposure to air, but is not readily oxidized by concentrated nitric acid at low temperature (+5°). Cf. §134, *d* and *e*.

136. Meta-chlorbenzaldehyde. Mix 20 g. of meta-nitrobenzaldehyde with a solution containing 90 g. of crystallized stannous chloride and 125 g. of fuming hydrochloric acid. The temperature may increase to such an extent that external cooling will be necessary. When the aldehyde has passed into solution, dilute the acid with water, and add sufficient ice to lower the temperature to 0°.

While you shake this mixture, pour into it, very slowly, a solution of 9.2 g. of sodium nitrite dissolved in 35 c.c. of water. Prepare a solution of cuprous chloride by boiling 6 g. of crystallized cupric chloride and 3 g. of copper turnings with 25 c.c. of hydrochloric acid and 6 c.c. of water. When this solution has been cooled to about 0°, pour the diazonium solution into it. (Cf. Sandmeyer's reaction.)

After 24 hours, distill the m-chlorbenzaldehyde with steam; separate the oil, and dry it with calcium chloride. Subject it to fractional distillation, and collect the fraction which boils between 210° and 216°. When this fraction is cooled in a freezing-mixture, it will yield solid m-chlorbenzaldehyde. The solid may be freed from oil by means of a Büchner funnel and a pump. It boils at 213°–214°; its melting-point is 17°–18°.

137. Stereoisomeric Aldoximes.

Meta-chlor- α -benzaldoxime. Dissolve 10 g. of m-chlorbenzaldehyde and 6 g. of hydroxylamine hydrochloride in 200 c.c. of water. Heat this mixture in a flask placed upon a water-bath. Pass a stream of carbon dioxide into the flask. (?) After several hours, cool the solution, and collect the crystalline oxime upon a filter. Recrystallize it from 95 per cent. alcohol. It melts at 70°–71°. It is also called meta-chlor-anti-benzaldoxime.

Conversion into Meta-chlor- β -benzaldoxime. Dissolve 5 g. of the oxime in 50 c.c. of dry ether, and conduct into it a stream of dry hydrogen chloride gas. (Cf. Appendix G.) The hydrochloride of the oxime will finally separate as a white crystalline solid. Collect this salt upon a filter protected as much as possible from moist air. Wash the salt with absolute ether, and dry it in a vacuum-desiccator over sulphuric acid.

To prepare the β -oxime itself, mix 5 g. of this hydrochloride with a solution of 2.5 g. of sodium carbonate in 25 c.c. of water. A colorless oil will form at first; after it is shaken, it will solidify.

Recrystallize the β -oxime from dilute alcohol. It is also called the syn-oxime. This solid will melt at 115° – 116° ; but, at the same time, it will be converted into the α -oxime. The fused substance, when it has solidified once more, will be found to melt at 70° – 71° , instead of 115° – 116° .

a. What is the significance of the terms syn and anti (α and β) as applied to aldioximes? How are space configurations chosen for two geometrical isomers?

Ketones.

138. Benzophenone. Friedel and Crafts' Reaction. In a 1-liter flask, mix 15 g. of anhydrous aluminium chloride with 50 c.c. of dry carbon disulphide. Through the stopper of this flask, pass a dropping-funnel and a bent adapter connected with a long condenser. At the upper end of this condenser, insert a calcium chloride tube bent downward and containing calcium chloride. From this tube there should be a long glass tube which reaches into a bottle and ends just above the surface of some water placed in the bottle. Into the dropping-funnel, pour a mixture of 15 g. of benzoyl chloride and 15 g. of dry benzene, and allow it to flow into the flask gradually. Heat the flask in a water-bath for two or three hours, or until the evolution of hydrogen chloride has practically ceased.

Remove the carbon disulphide by distillation in the usual way, and pour the residue into ice water. After adding 10 c.c. of concentrated hydrochloric acid, conduct steam into the product, and collect the distillate. Extract the ketone by means of ether, wash the ether with a solution of sodium hydroxide, and dry it. When the solvent has been removed subject the ketone to distillation. Use a small flask with a long side neck joined near the bulb, and without condenser attached to it. Benzophenone boils at 360° . Its melting-point is 48° .

139. Benzophenoneoxime. Dissolve 5 g. of benzophenone and 6 g. of hydroxylamine hydrochloride in 65 c.c. of alcohol and 40 c.c. of water. Add 10 g. of sodium hydroxide dissolved in 15 c.c. of water, and boil the mixture for about an hour in a flask attached to a reflux-condenser. Dilute the product with a large volume of water, and acidify it with dilute sulphuric acid. After several hours, collect the crystalline oxime, wash it with water, and dry it. The melting-point is 141° . The yield will be nearly quantitative. (Cf. § 31, Acetoxime.)

Beckmann's Rearrangement of a Ketoxime. Dissolve 3 g. of benzophenoneoxime in 40 c.c. of ether dried over sodium. In a closed weighing-bottle, weigh out 4 g. of phosphorus pentachloride in the form of a fine powder, and add it in small portions to the ether solution. Remove the ether by distillation, and pour the residue upon ice in a mortar. Grind the solid very fine, collect it upon a Büchner funnel, and wash it with water. When the benzanilid is dry, recrystallize it from boiling alcohol. The melting-point should be 162° .

a. How is this reaction employed to determine the space configurations of stereoisomeric ketoximes?

140. Benzophenone Phenylhydrazone. Dissolve 1.5 c.c. of phenylhydrazine in 5 c.c. of acetic acid (30 per cent.), and add to this solution 1 g. of benzophenone. The hydrazone will form readily when the mixture is thoroughly shaken. Collect it upon a filter and wash it. Dissolve it in a little hot alcohol and filter the solution if necessary. Add water to the filtrate until it shows a slight turbidity; then allow the solution to cool. The hydrazone will separate in crystalline form. It melts at 105° .

141. Quinones and Related Compounds.

a. Benzoquinone, Quinone. Dissolve 10 g. of aniline in a mixture of 54 g. of concentrated sulphuric acid and 200 c.c. of water. Cool this solution to about 10° , and add 6.4 g. of finely powdered potassium dichromate. This salt should be introduced slowly in one-gram portions. The operation should require about 20 minutes, during which the flask must be shaken very frequently. When all of the dichromate has been added, allow the flask to stand over night; then, with the conditions the same as before, add 13.5 g. of powdered potassium dichromate. The bluish color will finally change to brown.

Extract the solution repeatedly with ether. If an emulsion should form which prevents the separation of the layers, a few cubic centimeters of alcohol will cause the liquids to part. When the ether has been removed by distillation, impure quinone will be left.

The further purification of quinone may be accomplished by subjecting it to distillation in a current of steam. Place the solid in a distilling-flask, and conduct into it a rapid current of steam. Bright yellow crystals of quinone will collect in the condenser and in the receiver. It may be recrystallized from ligroin.

α . Notice the odor of quinone.

β . Add a few crystals of quinone to an acidulated solution of potassium iodide. What class of chemical compounds does quinone resemble in this reaction?

γ . Dissolve some quinone in chloroform, and add to it a solution of bromine in chloroform. What does this reaction suggest concerning the constitutional formula of quinone?

b. Reduction of Quinone to Hydroquinone. Dissolve 5 g. of quinone in 100 c.c. of commercial sodium bisulphite solution (40 per cent.). It may be necessary to warm the mixture slightly.* After cooling the reaction product, extract the solution repeatedly with ether. When the ether has been dried with anhydrous sodium sulphate, and removed by distillation, hydroquinone will be left as a slightly colored residue. It may be recrystallized from a little water containing sulphurous acid and animal charcoal to remove the color. The melting-point is 169° .

α . To an alkaline solution of hydroquinone, add an ammoniacal solution of silver nitrate.

β . Treat a concentrated solution of hydroquinone with ferric chloride. Try the same reaction with a dilute solution of hydroquinone and an excess of ferric chloride. Heat the mixture and observe the odor.

γ . **Acetyl Derivative, Hydroquinonediacetate.** Suspend some hydroquinone in twice its weight of acetic anhydride to which one drop of concentrated sulphuric acid has been added. Cool the product, collect the solid, and wash it with water.

δ . What structure formulæ have been proposed for quinone? Discuss the bearing of reactions α , β , and γ in both *a* and *b*, as evidence in support of, or in disproof of one or the other of these formulæ.

c. Dinitroso Resorcinol, Dichinoyldioxime.† Dissolve 5 g. of resorcinol in 20 c.c. of water containing 10 c.c. of concentrated hydrochloric acid, and 25 g. of sodium chloride. Cool the solution thoroughly by ice, and add slowly a cold solution of sodium nitrite containing 6.4 g. of sodium nitrite in 25 c.c. of water.

* *Note 11.* — As an alternative, suspend the quinone in a little water, and pass a rapid stream of sulphur dioxide into it until the solution becomes almost colorless.

† Hantzsch, Ber. **39**, 162.

After one hour, collect the precipitate, wash it with a little cold water, and dry it. Cf. § 126, Nitrosophenol. This compound is known as resorcin green or fast green, and is employed with iron salts as mordants to color cotton green; wool may be dyed green by it without a mordant.

CHAPTER XXV.

AROMATIC ACIDS AND THEIR DERIVATIVES.

142. Benzoic Acid by the Oxidation of Benzaldehyde.

Heat a few drops of benzaldehyde with an aqueous solution of potassium permanganate. What is the precipitate formed? When the odor of benzaldehyde has disappeared, add a few drops of alcohol to decompose any excess of permanganate. Filter the liquid and acidify the filtrate. Benzoic acid will be precipitated.

a. Are the processes usually employed in making benzoyl chloride, benzamide, benzoic ethyl ester similar in form to those which were used to make the corresponding derivatives of acetic acid?

143. Benzoic Anhydride. Dissolve equa-molecular quantities of benzoic acid and acetic anhydride in dry benzene, and boil the mixture for 6 hours. Subject the product to fractional distillation. The last fraction, which boils between 347° and 348° , is practically pure benzoic anhydride. The yield should be 80 per cent. (Kaufman and Luerbacher, Ber. **42**, 3483.)

a. How is nitrogen pentoxide usually prepared? Is there any analogy between this method and the method just described?

144. Benzoyl Peroxide.* Gradually dissolve some commercial sodium peroxide in a solution of sodium acetate, thoroughly cooled by crushed ice. Shake this solution with several drops of benzoyl chloride until a crystalline precipitate forms. Recrystallize the solid, using alcohol as the solvent. Benzoyl peroxide will be obtained. It will melt at 103° .

a. Heat a small sample of the solid.

b. Warm a little of it with an acidulated solution of potassium iodide. Explain your observation. Cf. § 134, Benzaldehyde, *c.*

* Pechman and Vanino, Ber. **27**, 1511.

145. Salicylic Acid from Oil of Wintergreen. Mix 1 g. of oil of wintergreen (methyl salicylate) with a solution of 2.5 g. of sodium hydroxide in 15 c.c. of water. Heat this mixture in a flask connected with a reflux-condenser. When all the oil has disappeared, acidify the solution, and separate the solid by filtration; dry the acid, and determine its melting-point.

a. How is salicylic acid obtained in large quantities?

b. How could you prepare oil of wintergreen synthetically? Heat some salicylic acid with soda lime. Observe the odor. What is formed?

c. To a dilute solution of salicylic acid, add a few drops of a very dilute solution of ferric chloride. What use is made of this reaction in detecting small amounts of salicylic acid; e.g., in foods?

146. Mandelic Acid Nitrile. Shake 15 g. of benzaldehyde with 50 c.c. of concentrated sodium hydrogen sulphite solution. Collect the addition product which forms, and wash it with a little water. Stir this substance with water enough to make a thick mixture, and pour into it a solution of 12 g. of potassium cyanide dissolved in 15 c.c. of water. When this mixture is stirred, the solid will go into solution, and an oil will form. This oil is the nitrile; it is very unstable.

a. **Mandelic Acid from its Nitrile.** Treat the nitrile with four times its weight of concentrated hydrochloric acid, and evaporate the mixture upon a water-bath until a crystalline film begins to form upon the surface of the liquid. When this solution has stood for several hours, collect the crystalline product, and extract the filtrate with ether to remove the remainder of the acid. Recrystallize the acid from water, or from benzene. Mandelic acid melts at 118°.

147. Gallic Acid.

a. Add a few drops of ferric chloride to a water solution of gallic acid.

b. **Rufigallic Acid.** Moisten a small amount of gallic acid with concentrated sulphuric acid. Warm the acid until the mixture turns deep red; then pour the product into a little cold water. Rufigallic acid is a derivative of anthraquinone. Cf. Alizarin.

c. Heat a little gallic acid in a dry test-tube. Does the liberated gas affect lime water? What are the chief products of decomposition?

148. Tannin.

a. Treat a water solution of tannin with a few drops of ferric chloride. How are "iron" inks made?

b. Soak a small piece of gelatine in cold water until it swells. Warm this gelatine with the water until it dissolves. Cool the solution and add tannin to it. What occurs? How is tannin employed in the tanning processes?

CHAPTER XXVI.

DERIVATIVES OF DIPHENYLMETHANE AND OF DIPHENYLETHANE.

149. Tetramethyl-p-diamidodiphenylmethane. Mix 1 c.c. of formalin solution with 10 c.c. of water, and add 0.5 c.c. of dimethylaniline. Acidify the mixture with dilute sulphuric acid and shake it vigorously for a few minutes. When this product has been made slightly alkaline by means of sodium hydroxide, boil it in a dish until the odor of dimethylaniline is no longer noticeable. Tetramethyl-p-diamidodiphenylmethane will be precipitated.

Collect this precipitate upon a small filter, and wash it with water. Spread the filter in a small porcelain dish; moisten it with dilute acetic acid, and sprinkle upon it some finely powdered lead dioxide. A blue dye (hydrole) will result. (?)

a. How is this reaction employed in similar cases as an intermediate stage in making various triphenylmethane dyes commercially?

150. Benzoïn. "Benzoïn Condensation." Dissolve 10 g. of benzaldehyde in 12 c.c. of alcohol, and add to it a solution of 1 g. of potassium cyanide in 10 c.c. of water. Connect the flask with a reflux-condenser, and heat this solution for 15 minutes. When the liquid has cooled, benzoïn will separate; it should be collected upon a filter, and crystallized from alcohol. It may be necessary to use a little animal charcoal to remove coloring matter. The melting-point is 134° .

a. Does benzoïn reduce Fehling's solution? Cf. §89, Monosaccharides.

151. Benzil. Mix 5 g. of benzoïn with 15 c.c. of concentrated nitric acid (sp. gr. 1.4). Shake the mixture frequently, and heat it upon a water-bath until oxides of nitrogen are no longer visible and a sample poured into water gives a precipitate which, when dissolved in alcohol, will not reduce Fehling's solution.

If this test shows no reduction, pour the acid solution in water, and collect the crystals upon a Büchner funnel. Recrystallize the benzil from alcohol. The melting-point is 95° .

a. What is benzilic acid? How is it obtained from benzil?

CHAPTER XXVII.

DERIVATIVES OF TRIPHENYLMETHANE — TRIPHENYLMETHANE DYES.

Triphenylmethane Dyes.

- **152. Malachite Green. (Leuco-base.)** Mix 10 g. of dimethylaniline, 4 g. of benzaldehyde, and 8 g. of anhydrous zinc chloride, and heat the mixture in a porcelain dish over a water-bath. This mixture should be stirred frequently, and a little water should be added to prevent it from becoming too thick by evaporation. After several hours, transfer the product to a flask, and remove the unchanged dimethylaniline by steam distillation. Cool this residue and pour away the solution of zinc chloride. Wash the impure leuco-base and dissolve it in hot absolute alcohol. Upon cooling, the leuco-base will separate in crystals, almost colorless. By repeated crystallization, it may be obtained colorless.
- **153. Malachite Green. (Dye.)** Dissolve 3 g. of the leuco-base in 36.3 c.c. of normal hydrochloric acid, and dilute the solution with 275 c.c. of water. Cool this solution, and add 2.2 g. of lead dioxide which has been suspended in 20 c.c. of water. This operation should require about 5 minutes. The mixture should be shaken for 5 minutes after all of the lead dioxide has been introduced.

Filter the solution, add 3.5 g. of zinc chloride, and then a sufficient amount of a saturated solution of salt to precipitate the dye so completely that a filtered sample of the mother liquor shows only a faint green color. Collect the dye and wash it with salt solution. It may be purified by dissolving it first in hot water, and then reprecipitating it by means of saturated salt solution. Finally, collect the dye, and dry it upon a piece of porous plate.

a. Treat a sample of malachite green with an excess of concentrated hydrochloric acid. (?) Add a large volume of water.

b. Add a solution of sodium hydroxide to a sample of malachite green. (?)

c. Treat a sample of the dye with zinc dust and hydrochloric acid. Explain these changes.

154. Parafuchsine, Pararosaniline Hydrochloride. (Dye.)

Mix 1 c.c. of aniline with 1 g. of p-toluidine and 3 g. of mercuric chloride. Heat this mixture to a temperature of 180°–200° for 15 minutes. Extract the residue with alcohol, filter the solution, and evaporate it. Make a water solution of the residue, and acidulate it with dilute hydrochloric acid.

a. Add concentrated hydrochloric acid to one portion of the solution. Explain the change in color. [R].

b. **Pararosaniline. (Color-base.)** To a second portion of the solution, add ammonium hydroxide or sodium hydroxide. The color will be removed. Explain this reaction.

c. **Paraleucaniline. (Leuco-base.)** To a third portion of the solution, add zinc dust, and warm the mixture. How is the color removed?

155. Rosolic Acid. Heat a mixture of 2 c.c. of phenol, 0.5 g. of oxalic acid, and 5 c.c. of concentrated sulphuric acid. Pour the red liquid into water, and add a slight excess of sodium hydroxide. The sodium salt of rosolic acid will be formed.

Phthaleïns.

156. Phenolphthaleïn. Mix a small crystal of phenol with an equal volume of powdered phthalic anhydride. Place the mixture in a small test-tube, moisten the powder with one drop of concentrated sulphuric acid, and heat the tube for three minutes in a bath whose temperature is about 160°. Cool the residue, dissolve it in about 2 c.c. of water, and add 1 c.c. of a 10 per cent. solution of sodium hydroxide. Filter the solution and pour the filtrate into water.

✓ **157. Fluoresceïn.** If resorcinol is substituted for phenol in preparation 156, and the other conditions are kept the same, fluoresceïn will be obtained. Notice the intense fluorescence of the water solution.

a. To some of the undiluted alkaline solution, add zinc dust, and shake the mixture. Filter the resulting solution and shake the filtrate with air. Compare azobenzol, pararosaniline, indoanilines, indigo.

✓ b. **Eosin.** Dissolve 6 g. of fluoresceïn in 20 c.c. of acetic acid, and add 4.5 g. of bromine dissolved in 18 c.c. of acetic acid. When the mixture is warmed, all of the substance will

pass into solution. The addition of water will cause the eosin to separate in red crystals.* Collect this solid, dry it, and recrystallize it from boiling alcohol. It will form crystals with one molecule of alcohol of crystallization. The yield should be about 8 g.

Eosin is not soluble in water. For dyeing purposes, it is necessary to convert it into one of its soluble salts, usually the sodium salt.

Mix 5 g. of eosin with 0.8 g. of sodium carbonate; moisten the mixture with a little alcohol and add 5 c.c. of water. Heat these substances on a water-bath until the evolution of carbon dioxide has ceased. Then add 15 c.c. of alcohol, heat the solution to boiling, and filter it while it is still hot. From the cold solution, a brown **sodium salt** of eosin will crystallize.

The **ammonium salt** of eosin may be made as follows:— Spread a thin layer of eosin upon a filter-paper placed over a dish containing concentrated ammonia water and covered with a funnel. The change will be complete when a sample of the solid will give a clear solution in water.

* *Note 12.*—Fluoresceïn paper—made by drying strips of paper which have been dipped in a solution containing 1 g. of fluoresceïn in 200 parts of 50 per cent. acetic acid—is frequently used to detect traces of bromine. Strips of the paper are lemon-yellow in color. They will assume a rose-pink hue when placed in bromine vapor.

CHAPTER XXVIII.

EXPERIMENTS IN DYEING.

158. Dyeing by Precipitation.

a. Chrom Yellow. Boil 10 small strips of cheese-cloth in a soap solution and rinse them thoroughly with water. Prepare two baths, one containing a solution of lead acetate, the other containing a solution of potassium dichromate. Heat these baths until they boil, and immerse a strip of cloth first in the bath containing lead acetate, then in the bath of potassium dichromate. Can the yellow color of the cloth be removed by washing it with water?

b. Indigo Dyeing. Grind 1 g. of natural indigo and 0.3 g. of ferrous sulphate with water in a mortar until a thin paste is formed. Pour this mixture into a wide-mouthed bottle (8 oz.) and add 0.4 g. of slaked lime. Fill the bottle with water and close it air-tight with a stopper. When the solution has become practically colorless, dip a strip of clean cheese-cloth into the solution and expose it to the air. Explain the reactions involved in this process.

159. Direct Dyes. Substantive Dyes for Cotton.

a. Congo Red, a Benzidine Dye. Dissolve 0.2 g. of Congo red in 50 c.c. of water, and add to it 0.2 g. of sodium carbonate dissolved in 20 c.c. of water; and 0.4 g. of sodium sulphate dissolved in 20 c.c. of water. Pour this mixture into a deep porcelain dish, and add 10 c.c. of water. When this bath is boiling, immerse strips of clean cheese-cloth in it, and continue the heating for one or two minutes. Rinse the strips thoroughly with water. Is the color "fast"?

b. Primuline, a Thiazol Dye. Dissolve 0.2 g. of primuline in 300 c.c. of water which contains 1.5 g. of sodium chloride and 0.3 g. of sodium carbonate.

Note 13. — In dyeing operations, salts used as sodium chloride in this case are often spoken of as "assistants". Cf. § 95, I, *c* and *d*; II, *c*. Are dyes in any way related to colloids?



Heat this bath and place in it three strips of clean cheese-cloth. Boil the bath 10 minutes. Can the color be removed by rinsing the cloth in water?

160. Developing the Color on the Fiber. Ingrain Colors.

a. Prepare the following baths:— (1) Dissolve 0.3 g. of sodium nitrite in 600 c.c. of cold water, and immediately before using the bath, add 3 c.c. of concentrated hydrochloric acid. (2) Dissolve 0.1 g. of sodium hydroxide in 25 c.c. of water and add 0.1 g. of β -naphthol. Heat the mixture until the naphthol dissolves and add 175 c.c. of water. (3) Dissolve 0.1 g. of resorcinol in a solution of 0.2 g. of sodium hydroxide in 25 c.c. of water. Then dilute this solution with 175 c.c. of water.

Place two strips of the cloth dyed in § 159, *b*, in the cold nitrite bath (1). After about 10 minutes, remove them and rinse them. Place one of these strips in bath (2) and the other in bath (3). This will develop the color. Wash the cloth with water and note the fastness of the color.

b. Para-nitraniline Red. Ice Colors. Printing. Mix 5 g. of β -naphthol with 5 g. of a solution of sodium hydroxide (sp. gr. 1.384 or 40° Baumé) and 25 c.c. of water. To this solution add 19 g. of Turkey red oil and 200 c.c. of water. Dip pieces of clean cheese-cloth in this bath. Place them upon a plate of glass, dry them partially with filter paper, and allow them to dry upon the glass support.

To make the diazo solution, dissolve 1.4 g. of *p*-nitraniline in 4 c.c. of concentrated hydrochloric acid and 4 c.c. of water. Add 5 g. of ice, and pour into it a solution of 0.7 g. of sodium nitrite in 5 c.c. of water. Stir the solution vigorously and allow it to stand for 30 minutes in ice; then filter it into a mixture containing 50 g. of starch-tragacanth, 5 g. of ice, and 2.5 g. of sodium acetate.

Note 14.— The starch tragacanth used as thickening may be made as follows:— Soak 50 g. of tragacanth in 1 liter of water for 12 hours. Heat it upon a water bath, and add a paste made by boiling an emulsion of 50 g. of starch in 300 c.c. of water and 200 c.c. of dilute acetic acid. Press this paste through a sieve.

If some of this thick diazo solution is placed upon the cloth treated with β -naphthol, the color will be developed, and will be found to be fast when the cloth is washed. To illustrate the process of printing, prepare a small beech-wood block, 4×4×3

inches, with one face planed smooth. By means of a brush with short bristles, coated with the thickened diazo solution, mark across the surface of the block first in one direction and then across these markings in the other direction. Carefully press the treated surface of the block upon a piece of prepared cloth placed upon a sheet of blotting paper, and strike the block with a hammer. When the cloth is rinsed with water, the color will develop.

161. Adjective Dyes for Cotton. Mordants. Lakes.

a. Basic Dyes. Prepare two baths, one containing 0.5 g. of tannic acid dissolved in 500 c.c. of water; a second containing 0.2 g. of tartar emetic dissolved in 200 c.c. of water. Dissolve about 0.1 g. of each of the following dyes in 200 c.c. of water: malachite green; fuchsine; methyl violet; methylene blue.

Boil the four baths containing the dyes, and place a strip of clean cheese-cloth in each one. After 5 minutes, remove the cloth strips and rinse them thoroughly in water. Is the color permanent? Heat woolen yarn and white silk in these dye baths, and rinse them thoroughly. Do these dyes act as substantive dyes towards wool and silk?

Boil the baths containing tannic acid and tartar emetic, and place four pieces of clean cloth first in the tannic acid bath. After 5 minutes, remove them and wring them. Now boil them for 5 minutes in the tartar emetic bath and wring them again. Immerse one piece in each of the boiling baths of the dyes and heat them 5 minutes. Can you remove the color by washing the strips?

b. Acid Dyes.

α. Alizarin. Mix 1 c.c. of alizarin paste, 1 g. of alizarin assistant (Turkey red oil), and 2.5 c.c. of 30 per cent. acetic acid with 125 c.c. of water. Heat the mixture to effect solution.

Add 5 c.c. of this alizarin solution, mixed with 100 c.c. of water, to each of the following solutions: 4 c.c. of aluminium sulphate solution; 2 c.c. of a saturated solution of chromic acetate; 2 c.c. of ferric chloride (1:10). To each solution, add 3 c.c. of normal sodium hydroxide.

Boil 50 c.c. of the alizarin solution and 500 c.c. of water in a deep porcelain dish, and immerse in this bath a strip of mordanted cloth prepared for alizarin dyeing. Such cloth may be obtained from any large dealer in chemical supplies.



✓ **β. Picric Acid, a Nitro-Dye.** Dissolve 2-3 g. of picric acid in a little hot water to which a few drops of sulphuric acid have been added. Place in this solution a piece of white woolen yarn, and a piece of white silk. After heating them for 1 minute, remove them from the bath, wring them, and dry them. Treat a piece of cheese-cloth in the same way. Are the colors fast in all cases?

To a solution of lead acetate, add an alum solution as long as a precipitate continues to form. After the solution has cleared, immerse a piece of cotton cloth in the solution, and dry it partially. Then place it in the hot picric acid bath for 1 minute. Wring the cloth and dry it. Is the color fast?

γ. Resorcin Green, a Quinone Oxime Dye. Try the action of a solution of this dye upon some white woolen yarn. Cf. § 141, c, Dinitroso Resorcin.

CHAPTER XXIX.

NAPHTHALENE AND ANTHRACENE.

Naphthalene.

162. α -Nitronaphthalene. Pour 5 g. of nitric acid (sp. gr. 1.33) upon 1 g. of naphthalene and allow the mixture to stand for 24 hours. Add water to dilute the acid, collect the precipitate and dry it. Pour upon it enough alcohol to moisten it, and add sufficient carbon disulphide to dissolve it with the exception of a small amount of dinitronaphthalene, which may be separated by filtration. Remove the solvent by distillation and recrystallize the nitro-compound from alcohol. The melting-point is 61° .

a. How could this compound be changed into α -naphthylamine? Cf. § 105, Aniline.

163. α - and β -Naphthol.

a. Shake a little α -naphthol with water; add sodium hydroxide, and shake the mixture again. If carbon dioxide is passed into the alkaline solution, what will occur?

b. How are these naphthols obtained? Does this method resemble the method used to prepare phenols?

c. **Martius's Yellow.** Dissolve 1 g. of α -naphthol in 4 c.c. of concentrated sulphuric acid and pour the mixture into 3 c.c. of concentrated nitric acid. 2,4-Dinitro- α -naphthol will be precipitated by the addition of water. Collect this precipitate upon a filter and wash it. It may be dissolved in dilute sodium hydroxide to give the **sodium salt** known as Martius's yellow. Such a solution will dye a piece of woolen yarn deep yellow.

164. β -Naphthol Methyl Ether. (Nerolin, Jara-Jara.)

Dissolve 5 g. of β -naphthol in a little methyl alcohol, and add 5 g. of methyl iodide and 2.5 g. of potassium hydroxide. Heat this mixture in a flask attached to a reflux-condenser. When the reaction is complete (?) remove the alcohol by distillation, and extract the potassium iodide from the residue by several treatments with water. Recrystallize the methyl ether from alcohol. Its melting-point is 72° . It is employed in making certain perfumes.

165. 1-Monobrom- β -Naphthol. Dissolve 5 g. of β -naphthol in a small amount of glacial acetic acid. To this concentrated solution, add the calculated amount of bromine necessary to form the monobromide. The bromine should be dissolved in an equal volume of glacial acetic acid, and should be added by means of a dropping-funnel while the β -naphthol solution is cooled and shaken. When the product has stood a short time, collect the crystals of the bromide, and wash them with water containing acetic acid. The melting-point is 84° .

Anthracene.

166. Anthracene Picrate. Mix a solution of anthracene in glacial acetic acid with an equal amount of a solution of picric acid in the same solvent. Red crystals of the picric acid addition product will be formed. They melt at 138° .

167. Anthraquinone. Pour 40 c.c. of glacial acetic acid into a flask containing 5 g. of anthracene. Connect the flask with a reflux-condenser, and heat it in a bath of boiling water. Dissolve 9 g. of chromic anhydride^{*} (CrO_3) in a very little water, and add it to 13 c.c. of glacial acetic acid. Gradually pour this solution through the condenser-tube into the flask. When the mixture has boiled for 5 minutes or so, pour the solution into water. Collect the precipitate, wash it, and dry it. It may be recrystallized from glacial acetic acid, or from toluene. The melting-point is 273° .

a. How can anthraquinone be changed into anthracene? What historical significance does this change have?

b. How is alizarin made from anthraquinone?

c. Warm a small amount of anthraquinone with zinc dust and sodium hydroxide. Filter the solution and shake it with air. (?)

DIVISION 2. HETEROCYCLIC COMPOUNDS.

CHAPTER XXX.

HETEROCYCLIC COMPOUNDS: — METHYL-PHENYLPYRAZOLONE;
INDIGO; PYRIDINE; QUINOLINE.

Heterocyclic Compounds.

168. Methyl-phenylpyrazolone. In a large test-tube, mix 5 g. of phenylhydrazine and 6.3 g. of freshly distilled acetoacetic ethyl ester. Cool the mixture during the first part of the process. After several hours, separate the water which has formed, and heat the oily condensation product (?) for two hours upon a water-bath. To remove foreign coloring matter, pour the warm liquid into a little ether. Collect the crystals which separate and wash them with ether. By the slow evaporation of an alcoholic solution placed in a loosely covered Erlenmeyer flask, fine crystals, melting at 127° , may be obtained.

a. To a solution of the pyrazolone derivative in boiling water, add ferric chloride. The blue color is caused by **pyrazol blue**, which may be extracted by means of chloroform. Delicacy, 1 : 10,000. Cf. §169, Indigo Blue.

b. Treat some of the methyl-phenylpyrazolone with hydrochloric acid. It will dissolve. To the acid solution, add sodium hydroxide enough to neutralize the acid; then add an excess. Explain these reactions.

c. What is antipyrene? How is it obtained from methyl-phenylpyrazolone?

169. Indigo. Indigo blue.

a. Heat a little indigo carefully in a dry test-tube. What occurs?

b. Dissolve a small amount of indigo in hot nitrobenzene, and allow it to separate.

c. Mix 2 g. of indigo with 4 g. of powdered sodium hydroxide. Place this mixture in a hard-glass test-tube and subject it to dry distillation. Aniline will be formed. Make tests to prove that the distillate contains aniline. What is the origin of the term aniline?

d. Indigo Sulphonic Acid. Indigo Carmine. Heat 0.2 g. of indigo with 2 c.c. of fuming sulphuric acid. Pour the cooled solution into water.

e. Reduction of Indigo. Indigo White. (Cf. §158, Dyeing.)

f. Heat a small amount of indigo or indigo sulphonic acid with concentrated nitric acid. Isatin is produced.

170. Synthesis of Indigo from Ortho-nitrobenzaldehyde.

To 1 c.c. of water containing a drop or two of acetone, add a few small crystals of o-nitrobenzaldehyde, and warm the liquid to a temperature of 50°, but not above this point. Cool the solution and add a few drops of a 10 per cent. solution of sodium hydroxide. At first the liquid will assume a yellow hue, which will soon become green, and finally, blue. Chloroform will extract the indigo.

171. Pyridine.

a. Make a water solution of pyridine and test it with neutral litmus paper. Explain the result.

b. Add some of the clear pyridine solution to solutions of ferric chloride and of aluminium chloride.

c. Mix a few drops of pyridine with an equal volume of methyl iodide. A solid is formed, and heat is evolved. (?) To what class of amines does pyridine belong? What is the compound produced by the action of methyl iodide upon pyridine? Cf. §85, Tetraethylammonium Bromide.

172. Quinoline. Skraup's Synthesis. Mix 6 g. of nitrobenzene, 9.5 g. of aniline, and 30 g. of dehydrated glycerol, obtained by heating glycerol in an open dish at 175°. Place the mixture in a round-bottomed flask (1 liter) and add 25 g. of concentrated sulphuric acid. Shake the flask during this process.

Connect the flask with a reflux-condenser, and heat it over a wire gauze until a rapid evolution of water-vapor commences, when the flame should be removed at once. When the first violent reaction has abated, continue to boil the mixture for 1 hour. It should then be diluted with water and distilled in a current of steam to remove nitrobenzene.

Make the remaining solution distinctly alkaline, and subject it to distillation with steam until the quinoline and unchanged aniline have collected in the receiver; add hydrochloric acid to the distillate to dissolve the quinoline and aniline; and treat this solution with an excess of sodium nitrite, which, by diazotizing

the aniline salt, will eliminate this impurity. Boil this solution until the diazo-compound is entirely destroyed. (?)

After adding sodium hydroxide in excess, distill the quinoline with steam, and then extract it with ether. When the ether has been removed as usual, dry the quinoline with solid potassium hydroxide, and distill it. The boiling-point is 237° .

a. Dissolve one or two drops of quinoline in hydrochloric acid, and add a solution of hydrochlorplatinic acid. The chlorplatinate will form; it may be recrystallized from boiling dilute hydrochloric acid.

b. Dissolve two or three drops of quinoline in dilute hydrochloric acid, and add a solution of potassium dichromate. Quinoline dichromate will be formed.

CHAPTER XXXI.

METALLO-ORGANIC COMPOUNDS.

173. Zinc Ethyl or Zinc Methyl. (Lachman, Am. Ch. J. 24, 31 (1900).) Make an intimate mixture of 25 g. of zinc dust and 3 g. of powdered copper oxide. After placing this mixture loosely in a short combustion-tube, pass a stream of dry hydrogen gas over it, and heat the mixture just to dull redness for 20 minutes. Allow the product to cool in a stream of hydrogen.

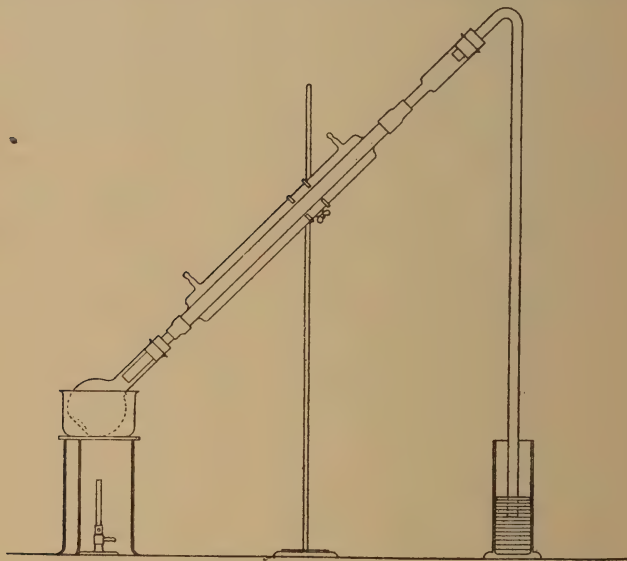


Fig. 22.

After placing this "zinc-copper-couple" in a small round-bottomed flask together with 25 g. of ethyl iodide, or of methyl iodide, connect the flask by means of a bent adapter with a dry

reflux-condenser. When the air in the apparatus has been replaced by dry carbon dioxide, and access of air to the condenser has been prevented by a mercury valve, the mixture of iodide and zinc should be heated on a water-bath until drops of the iodide cease to run back from the condenser. What gas escapes during this operation?

After the condenser has been inverted, and a suitable receiver has been provided, a stream of carbon dioxide, carefully dried over phosphorus pentoxide, should be allowed to flow through the entire apparatus before commencing the distillation. (Cf. Appendix G.) The flask may now be immersed carefully in an oil-bath (or metal-bath) which should be heated gradually while the zinc alkyl distills until it reaches a temperature of 150° ; the temperature may be increased finally to 180° .

The zinc alkyl may be purified by a second distillation in a stream of carbon dioxide. Owing to its spontaneous inflammability, it is a dangerous substance to handle, or to keep; it is usually preserved in sealed glass tubes, or small flasks with tight cork stoppers. All operations with zinc alkyls must be carried out in an atmosphere of some indifferent gas. If a rapid stream of dry carbon dioxide is conducted into a large glass beaker or jar, it is possible to work with zinc alkyls at the bottom of such a vessel without danger. Make the following tests:—

a. Allow a drop of zinc ethyl to come into contact with air.

b. Fill a small glass bulb with the zinc alkyl (Instructions). Seal the stem, and place the bulb in a vessel of water; cover the bulb with a cylinder of water, and by pressing the rim of the cylinder upon the stem of the bulb, cause the stem to break. What is formed? What is the white insoluble substance?

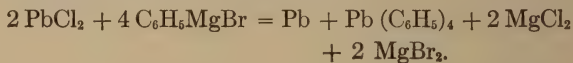
c. What are some of the applications which have been made of zinc alkyls in chemical synthesis? [R]. What is Grignard's synthesis? What advantages does Grignard's method have that are not possessed by the similar methods requiring zinc alkyls?

174. Lead Tetraphenyl.* Grignard's Synthesis. To 70 g. of ether, thoroughly dried over metallic sodium, add 25 g. of bromobenzene and 3.7 g. of metallic magnesium. Close the flask with a calcium chloride tube and allow it to stand 24 hours in a dish containing water. By this process, phenyl magnesium bromide

* Pfeiffer and Truskier, Ber. **37**, 1127.

will be formed. Cf. §15, Tertiary Butyl Alcohol. When the magnesium has disappeared, add 24 g. of dry, carefully powdered lead chloride. The chloride should be added in small portions. Allow this mixture to stand 2 days. Shake it occasionally.

Add 200 c.c. of water faintly acidulated with hydrochloric acid. Collect the dark precipitate upon a Büchner funnel, and dry it thoroughly. Place the dry solid in a flask connected with a reflux-condenser. Boil it with 100 c.c. of benzol, and filter the benzene through a folded filter, but leave the solid in the flask. Repeat the extraction with benzene. Combine the filtrates, and concentrate them until the volume is about 75 c.c. When this solution cools, lead tetraphenyl will separate in colorless needles, which melt at 222°.



APPENDICES.

APPENDIX A. TEMPERATURE MEASUREMENT AND HEAT UNITS. HEAT VALUE.

TABLE I. — Interconversion of Thermometric Readings on
the Centigrade and Fahrenheit Scales.

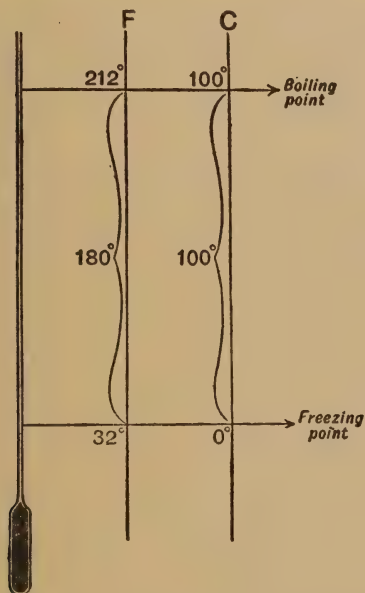


Fig. 23.

GENERAL FORMULAE.

C. = Centigrade; F. = Fahrenheit.

$$t^{\circ} \text{ C.} = \frac{9}{5} \cdot t + 32^{\circ} \text{ F.}$$

$$t^{\circ} \text{ F.} = \frac{5}{9} \cdot (t - 32)^{\circ} \text{ C.}$$

TABLE OF CENTIGRADE AND FAHRENHEIT DEGREES.

| Deg. C. | Deg. F. | Deg. C. | Deg. F. | Deg. C. | Deg. F. | Deg. C. | Deg. F. | Deg. C. | Deg. F. |
|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| 0 | 32.0 | 21 | 69.8 | 41 | 105.8 | 61 | 141.8 | 81 | 177.8 |
| 1 | 33.8 | 22 | 71.6 | 42 | 107.6 | 62 | 143.6 | 82 | 179.6 |
| 2 | 35.6 | 23 | 73.4 | 43 | 109.4 | 63 | 145.4 | 83 | 181.4 |
| 3 | 37.4 | 24 | 75.2 | 44 | 111.2 | 64 | 147.2 | 84 | 183.2 |
| 4 | 39.2 | 25 | 77.0 | 45 | 113.0 | 65 | 149.0 | 85 | 185.0 |
| 5 | 41.0 | 26 | 78.8 | 46 | 114.8 | 66 | 150.8 | 86 | 186.8 |
| 6 | 42.8 | 27 | 80.6 | 47 | 116.6 | 67 | 152.6 | 87 | 188.6 |
| 7 | 44.6 | 28 | 82.4 | 48 | 118.4 | 68 | 154.4 | 88 | 190.4 |
| 8 | 46.4 | 29 | 84.2 | 49 | 120.2 | 69 | 156.2 | 89 | 192.2 |
| 9 | 48.2 | 30 | 86.0 | 50 | 122.0 | 70 | 158.0 | 90 | 194.0 |
| 10 | 50.0 | 31 | 87.8 | 51 | 123.8 | 71 | 159.8 | 91 | 195.8 |
| 11 | 51.8 | 32 | 89.6 | 52 | 125.6 | 72 | 161.6 | 92 | 197.6 |
| 12 | 53.6 | 33 | 91.4 | 53 | 127.4 | 73 | 163.4 | 93 | 199.4 |
| 13 | 55.4 | 34 | 93.2 | 54 | 129.2 | 74 | 165.2 | 94 | 201.2 |
| 14 | 57.2 | 35 | 95.0 | 55 | 131.0 | 75 | 167.0 | 95 | 203.0 |
| 15 | 59.0 | 36 | 96.8 | 56 | 132.8 | 76 | 168.8 | 96 | 204.8 |
| 16 | 60.8 | 37 | 98.6 | 57 | 134.6 | 77 | 170.6 | 97 | 206.6 |
| 17 | 62.6 | 38 | 100.4 | 58 | 136.4 | 78 | 172.4 | 98 | 208.4 |
| 18 | 64.4 | 39 | 102.2 | 59 | 138.2 | 79 | 174.2 | 99 | 210.2 |
| 19 | 66.2 | 40 | 104.0 | 60 | 140.0 | 80 | 176.0 | 100 | 212.0 |
| 20 | 68.0 | | | | | | | | |

TABLE II. — Corrections to Apply to Melting-points and Boiling-points for Emerging Stem and Changes in Pressure.

For the determination of accurate melting-points and boiling-points, a standard thermometer should be used. If the thread of mercury is partially outside of the heated bath (melting-point) or of the vapor (boiling-point), a correction must be added

to the observed reading in degrees. The following formula may be used to calculate this correction:

$$\text{Correction} = N (T - t) \times 0.000154.$$

T = apparent temperature in degrees Centigrade registered by the main thermometer.

N = length of mercury column in degrees above the surface of the heated bath or vapor.

t = temperature of a second thermometer, the bulb of which is placed at half the length of N above the surface of the bath or vapor.

0.000154 = the apparent expansion of mercury in glass for 1°C .

TABLE OF CORRECTIONS TO BE ADDED FOR DIFFERENT
VALUES OF N AND $T - t$.

| N. | $T - t = 10^\circ$ | 20° | 40° | 50° | 60° | 80° | 100° | 120° |
|-----|--------------------|------------|------------|------------|------------|------------|-------------|-------------|
| 10 | 0.02 | 0.03 | 0.06 | 0.08 | 0.09 | 0.12 | 0.15 | 0.18 |
| 20 | 0.03 | 0.06 | 0.12 | 0.15 | 0.18 | 0.25 | 0.31 | 0.37 |
| 40 | 0.06 | 0.12 | 0.25 | 0.31 | 0.37 | 0.50 | 0.62 | 0.74 |
| 60 | 0.09 | 0.18 | 0.37 | 0.46 | 0.56 | 0.74 | 0.92 | 1.11 |
| 80 | 0.12 | 0.25 | 0.50 | 0.62 | 0.74 | 0.99 | 1.23 | 1.48 |
| 100 | 0.15 | 0.31 | 0.62 | 0.77 | 0.92 | 1.23 | 1.54 | 1.85 |
| 120 | 0.18 | 0.37 | 0.74 | 0.92 | 1.11 | 1.48 | 1.85 | 2.26 |
| 140 | 0.22 | 0.43 | 0.86 | 1.08 | 1.39 | 1.72 | 2.16 | 2.59 |
| 160 | 0.25 | 0.49 | 0.99 | 1.23 | 1.48 | 1.97 | 2.46 | 2.96 |
| 180 | 0.28 | 0.56 | 1.11 | 1.39 | 1.66 | 2.22 | 2.77 | 3.33 |
| 200 | 0.31 | 0.62 | 1.23 | 1.54 | 1.85 | 2.46 | 3.08 | 3.70 |

This correction may be avoided by using a short thermometer the stem of which is completely immersed in the bath or vapor.

In the determination of boiling-points, an additional correction must be made for variations in pressure if the boiling-points at 760 mm. are desired. At pressures varying between 720 and 780, this correction will be approximately 0.1°C . for every 2.7 mm. It will have the plus (+) sign below 760 mm. and the minus (-) sign with higher pressures. For such slight changes in pressure, no correction for melting-points need be applied, since for such variations the correction is negligible.

TABLE III. — Table of Freezing-mixtures of Snow or Powdered Ice and Various Substances.

100 parts of snow at -1° mixed with the indicated weight of the following substances will give the temperature shown in the third column.

| Substance. | Parts by weight. | Temp. Deg. |
|---|------------------|------------|
| Potassium sulphate..... | 10 | -1.9 |
| Sodium carbonate crys..... | 20 | -2.0 |
| Potassium nitrate..... | 13 | -2.85 |
| Potassium chloride..... | 30 | -10.9 |
| Ammonium chloride..... | 25 | -15.4 |
| Ammonium nitrate..... | 45 | -16.75 |
| Sodium nitrate..... | 50 | -21.3 |
| Sodium chloride..... | 30 | -22.4 |
| Calcium chloride crys. ($\text{CaCl}_2 + 2 \text{H}_2\text{O}$).. | 143 | -50 |
| Solid carbon dioxide and ether | | -100 |

TABLE IV. — Comparison of the Various Heat Units.

At the present time, several different heat units are employed to designate quantity of heat. The following ones are most frequently used:—

a. The Gram Calorie (Small Calorie), cal., is equal to the amount of heat absorbed by one gram of water in warming one degree C. This quantity, however, is not the same for all 1° intervals; e.g., the amount of heat necessary to warm a gram of water from 0° to 1° is a somewhat different value from that which is required to heat it from 99° to 100° . Practically, the calorie measured between 15° and 16° is the most convenient.

1 gram calorie = 42,720 gram centimeters (mechanical equivalent of heat).

b. The Kilogram Calorie (Large Calorie), Cal., is the amount of heat required to raise the temperature of one kilogram of water 1° C. Here, again, it will be evident that this quantity will vary with the different unit intervals chosen.

c. The British Thermal Unit, B.T.U., is quite generally employed in engineering work in America and in England. It may be defined as the amount of heat necessary to raise the

temperature of one pound of water 1° F. Since 1 pound is equal to 453.6 g., and 1° F. is equivalent to $\frac{5}{9}^{\circ}$ C., it follows that

$$1 \text{ B.T.U.} = 453.6 \times \frac{5}{9} = 252 \text{ gram calories.}$$

Consequently

$$1 \text{ Cal.} = 1000 \text{ cal.} = 3.97 \text{ B.T.U.}$$

$$1 \text{ B.T.U.} = 252 \text{ cal.} = 0.252 \text{ Cal.}$$

$$1 \text{ cal.} = 0.001 \text{ Cal.} = 0.00397 \text{ B.T.U.}$$

Heat Value, Calorific Power, Heat of Combustion are expressed in calories per gram or in B.T.U.'s per pound of substance. It is evident that the unit of mass in comparing these two numerical values will cancel; and in consequence, one calorie per gram (cal.) may be read as $\frac{2}{3}$ B.T.U.'s per pound. Thus, although the absolute value of 1000 cal. in quantity of heat is 3.97 B.T.U.'s, a heat value of 1000 cal. per gram may be read as 1800 B.T.U.'s per pound.

APPENDIX B. PRESSURE MEASUREMENT.

TABLE V. — Correction of Barometric Readings.

To reduce the reading taken at room temperature (Temperature) to the corresponding height of a column of mercury at 0°, subtract the proper number in the second column (Correction) from the actual reading in millimeters.

| Tempera- ture. Deg. | Correction. | Tempera- ture. Deg. | Correction. | Tempera- ture. Deg. | Correction. |
|---------------------------|-------------|---------------------------|-------------|---------------------------|-------------|
| 12 | 1.6 | 17 | 2.2 | 23 | 3.0 |
| 13 | 1.7 | 18.5 | 2.4 | 24.5 | 3.2 |
| 14 | 1.8 | 20 | 2.6 | 25 | 3.3 |
| 15 | 2.0 | 21.5 | 2.8 | 26 | 3.4 |

TABLE VI. — Tension of Aqueous Vapor in Millimeters.

| Tempera- ture. Deg. | Pressure. | Tempera- ture. Deg. | Pressure. | Tempera- ture. Deg. | Pressure. |
|---------------------------|-----------|---------------------------|-----------|---------------------------|-----------|
| 0 | 4.6 | 16 | 13.5 | 26 | 25.1 |
| 5 | 6.5 | 17 | 14.4 | 27 | 26.5 |
| 8 | 8.0 | 18 | 15.4 | 28 | 28.1 |
| 9 | 8.6 | 19 | 16.3 | 29 | 29.8 |
| 10 | 9.2 | 20 | 17.4 | 30 | 31.8 |
| 11 | 9.8 | 21 | 18.5 | 31 | 33.4 |
| 12 | 10.5 | 22 | 19.7 | 32 | 35.4 |
| 13 | 11.2 | 23 | 20.9 | 33 | 37.4 |
| 14 | 11.9 | 24 | 22.2 | 34 | 39.6 |
| 15 | 12.7 | 25 | 23.6 | 100 | 760.0 |

APPENDIX C. VOLUME AND WEIGHT RELATIONS. SPECIFIC GRAVITY.

By **specific gravity** * of a liquid is meant its relative weight compared with the weight of an equal volume of pure water at some definite temperature. Since the density of a liquid varies as its temperature changes, the scale is adjusted to a certain temperature, usually 15°C. with water at $15^{\circ} = 1$. In some of the following tables the values are based upon water at 15° . In order to transpose these values to the basis of water at its greatest density ($+4^{\circ}$), it will be necessary to multiply the values in such tables by 0.99916.

Two other scales are still in use in technical work; viz., the Baumé and the Twaddell.

Baumé. On the Baumé hydrometer, the scale readings bear no direct relation to actual specific gravity. Baumé dissolved 15 parts of pure sodium chloride in 85 parts of water at 12.5°C. The point to which his instrument sank in this solution was marked 15, while the point to which it sank when placed in pure water was marked 0. The distance between these two points was divided into 15 equal parts, and the stem was calibrated in divisions of this width. The divisions are called degrees.

In the case of liquids lighter than water, the point to which the instrument sank in a 10 per cent. solution of sodium chloride solution was marked 0; while the point to which it sank in pure water was marked 10. The distance between these two points was divided into 10 equal parts, and the stem was graded in equal divisions through its entire length. This instrument is extremely unscientific in principle. Thus, since the 0 is placed at the bottom of the stem, the lighter the gravity of the liquid the greater numerically is the scale reading; e.g., a liquid reading 70 Bé. is of a less density than one of 50 Bé., which, in turn, is lighter than water at 10 Bé.

* This account, slightly modified, is taken from Thorp's "Outlines of Industrial Chemistry."

Twaddell's Hydrometer. The spindle of Twaddell's hydrometer is graduated from 1 to 174. The readings are direct. The reading of pure water at 15.5° C. is taken as 0, and each subsequent rise of 0.005 in specific gravity is recorded on the scale as one additional division. Thus, 10 Twaddell becomes a specific gravity of 1.050. The divisions are spoken of as degrees.

Interconversion of Various Scale Values. Tw. = reading Twaddell; Bé. = reading Baumé; Sp. gr. = Specific gravity.

$$\text{Sp. gr.} = \frac{144.3}{144.3 - \text{Bé.}} \text{ for liquids heavier than water. } 15^\circ \text{ C.}$$

$$\text{Sp. gr.} = \frac{140}{130 + \text{Bé.}} \text{ for liquids lighter than water. } 17.5^\circ \text{ C.}$$

$$\text{Sp. gr.} = 1 + (\text{Tw.} \times 0.005) \quad 15.5^\circ \text{ C.}$$

TABLE VII. — Table of Specific Gravity and Percentage of Sodium Hydroxide in Aqueous Solutions.

SPECIFIC GRAVITY AT 15° COMPARED WITH WATER AT 15° = 1.
(Lunge.)

| Sp. Gr. | Baumé. | Proc. NaOH. | Sp. Gr. | Baumé. | Proc. NaOH. |
|---------|--------|-------------|---------|--------|-------------|
| 1.007 | 1 | 0.61 | 1.220 | 26 | 19.58 |
| 1.014 | 2 | 1.20 | 1.231 | 27 | 20.59 |
| 1.022 | 3 | 2.00 | 1.241 | 28 | 21.42 |
| 1.029 | 4 | 2.71 | 1.252 | 29 | 22.64 |
| 1.036 | 5 | 3.35 | 1.263 | 30 | 23.67 |
| 1.045 | 6 | 4.00 | 1.274 | 31 | 24.81 |
| 1.052 | 7 | 4.64 | 1.285 | 32 | 25.80 |
| 1.060 | 8 | 5.29 | 1.297 | 33 | 26.83 |
| 1.067 | 9 | 5.87 | 1.308 | 34 | 27.80 |
| 1.075 | 10 | 6.55 | 1.320 | 35 | 28.83 |
| 1.083 | 11 | 7.31 | 1.332 | 36 | 29.93 |
| 1.091 | 12 | 8.00 | 1.345 | 37 | 31.22 |
| 1.100 | 13 | 8.68 | 1.357 | 38 | 32.47 |
| 1.108 | 14 | 9.42 | 1.370 | 39 | 33.69 |
| 1.116 | 15 | 10.06 | 1.383 | 40 | 34.96 |
| 1.125 | 16 | 10.97 | 1.397 | 41 | 36.25 |
| 1.134 | 17 | 11.84 | 1.410 | 42 | 37.47 |
| 1.142 | 18 | 12.64 | 1.424 | 43 | 38.80 |
| 1.152 | 19 | 13.55 | 1.438 | 44 | 39.99 |
| 1.162 | 20 | 14.37 | 1.453 | 45 | 41.41 |
| 1.171 | 21 | 15.13 | 1.468 | 46 | 42.83 |
| 1.180 | 22 | 15.91 | 1.483 | 47 | 44.38 |
| 1.190 | 23 | 16.77 | 1.498 | 48 | 46.15 |
| 1.200 | 24 | 17.67 | 1.514 | 49 | 47.60 |
| 1.210 | 25 | 18.58 | 1.530 | 50 | 49.02 |

TABLE VIII. — Table of Specific Gravity and Percentage Composition of Ammonia in Aqueous Solution.

The correction values in the fourth column hold for the temperature interval 13–17°. For example, if the specific gravity at 13° were found to be 0.900, the specific gravity at 15° would be less, and would be found by subtracting $2 \times 0.00057 = 0.001$ from the value observed. This would give for the specific gravity 0.899, or an ammonia content about one-third of one per cent. higher.

SPECIFIC GRAVITY AT 15° COMPARED WITH WATER AT 15° = 1.
(*Lunge and Wiernik.*)

| Sp. Gr. | Proc. NH ₃ . | 1 l. contains NH ₃ at 15° g. | Correction for ± 1°. | Sp. Gr. | Proc. NH ₃ . | 1 l. contains NH ₃ at 15° g. | Correction for ± 1°. |
|---------|-------------------------|--|----------------------|---------|-------------------------|--|----------------------|
| 1.000 | 0.00 | 0.0 | 0.00018 | 0.940 | 15.63 | 146.9 | 0.00039 |
| 0.998 | 0.45 | 4.5 | 0.00018 | 0.938 | 16.22 | 152.1 | 0.00040 |
| 0.996 | 0.91 | 9.1 | 0.00019 | 0.936 | 16.82 | 157.4 | 0.00041 |
| 0.994 | 1.37 | 13.6 | 0.00019 | 0.934 | 17.42 | 162.7 | 0.00041 |
| 0.992 | 1.84 | 18.2 | 0.00020 | 0.932 | 18.03 | 168.1 | 0.00042 |
| 0.990 | 2.31 | 22.9 | 0.00020 | 0.930 | 18.64 | 173.4 | 0.00042 |
| 0.988 | 2.80 | 27.7 | 0.00021 | 0.928 | 19.25 | 178.6 | 0.00043 |
| 0.986 | 3.30 | 32.5 | 0.00021 | 0.926 | 19.87 | 184.2 | 0.00044 |
| 0.984 | 3.80 | 37.4 | 0.00022 | 0.924 | 20.49 | 189.3 | 0.00045 |
| 0.982 | 4.30 | 42.2 | 0.00022 | 0.922 | 21.12 | 194.7 | 0.00046 |
| 0.980 | 4.80 | 47.0 | 0.00023 | 0.920 | 21.75 | 200.1 | 0.00047 |
| 0.978 | 5.30 | 51.8 | 0.00023 | 0.918 | 22.39 | 205.6 | 0.00048 |
| 0.976 | 5.80 | 56.6 | 0.00024 | 0.916 | 23.03 | 210.9 | 0.00049 |
| 0.974 | 6.30 | 61.4 | 0.00024 | 0.914 | 23.68 | 216.3 | 0.00050 |
| 0.972 | 6.80 | 66.1 | 0.00025 | 0.912 | 24.33 | 221.9 | 0.00051 |
| 0.970 | 7.31 | 70.9 | 0.00025 | 0.910 | 24.99 | 227.4 | 0.00052 |
| 0.968 | 7.82 | 75.7 | 0.00026 | 0.908 | 25.65 | 232.9 | 0.00053 |
| 0.966 | 8.33 | 80.5 | 0.00026 | 0.906 | 26.31 | 238.3 | 0.00054 |
| 0.964 | 8.84 | 85.2 | 0.00027 | 0.904 | 26.98 | 243.9 | 0.00055 |
| 0.962 | 9.35 | 89.9 | 0.00028 | 0.902 | 27.65 | 249.4 | 0.00056 |
| 0.960 | 9.91 | 95.1 | 0.00029 | 0.900 | 28.33 | 255.0 | 0.00057 |
| 0.958 | 10.47 | 100.3 | 0.00030 | 0.898 | 29.01 | 260.5 | 0.00058 |
| 0.956 | 11.03 | 105.4 | 0.00031 | 0.896 | 29.69 | 266.0 | 0.00059 |
| 0.954 | 11.60 | 110.7 | 0.00032 | 0.894 | 30.37 | 271.5 | 0.00060 |
| 0.952 | 12.17 | 115.9 | 0.00033 | 0.892 | 31.05 | 277.0 | 0.00060 |
| 0.950 | 12.74 | 121.0 | 0.00034 | 0.890 | 31.75 | 282.6 | 0.00061 |
| 0.948 | 13.31 | 126.2 | 0.00035 | 0.888 | 32.50 | 288.6 | 0.00062 |
| 0.946 | 13.88 | 131.3 | 0.00036 | 0.886 | 33.25 | 294.6 | 0.00063 |
| 0.944 | 14.46 | 136.5 | 0.00037 | 0.884 | 34.10 | 301.4 | 0.00064 |
| 0.942 | 15.04 | 141.7 | 0.00038 | 0.882 | 34.95 | 308.3 | 0.00065 |

TABLE IX. — Table of Specific Gravity and Percentage Composition of Hydrochloric Acid at 15° C. Water at 4° = 1.*(Lunge and Marchlewski.)*

| Sp. gr. 15° 4° in vacuo. | Per cent. HCl by weight. | Sp. gr. 15° 4° in vacuo. | Per cent. HCl by weight. | Sp. gr. 15° 4° in vacuo. | Per cent. HCl by weight. |
|-----------------------------------|--------------------------------|-----------------------------------|--------------------------------|-----------------------------------|--------------------------------|
| 1.000 | 0.16 | 1.075 | 15.16 | 1.150 | 29.57 |
| 1.005 | 1.15 | 1.080 | 16.15 | 1.155 | 30.55 |
| 1.010 | 2.14 | 1.085 | 17.13 | 1.160 | 31.52 |
| 1.015 | 3.12 | 1.090 | 18.11 | 1.165 | 32.49 |
| 1.020 | 4.13 | 1.095 | 19.06 | 1.170 | 33.46 |
| 1.025 | 5.15 | 1.100 | 20.01 | 1.175 | 34.42 |
| 1.030 | 6.15 | 1.105 | 20.97 | 1.180 | 35.39 |
| 1.035 | 7.15 | 1.110 | 21.92 | 1.185 | 36.31 |
| 1.040 | 8.16 | 1.115 | 22.86 | 1.190 | 37.23 |
| 1.045 | 9.16 | 1.120 | 23.82 | 1.195 | 38.16 |
| 1.050 | 10.17 | 1.125 | 24.78 | 1.200 | 39.11 |
| 1.055 | 11.18 | 1.130 | 25.75 | | |
| 1.060 | 12.19 | 1.135 | 26.70 | | |
| 1.065 | 13.19 | 1.140 | 27.66 | | |
| 1.070 | 14.17 | 1.145 | 28.61 | | |

TABLE X. — Table of Specific Gravity and Percentage Composition of Solutions of Sulphuric Acid at 15° C. Water at 4° = 1.*(Lunge and Isler.)*

| Sp. gr. 15° 4° in vacuo. | 100 parts by weight con- tains per cent. H ₂ SO ₄ . | Sp. gr. 15° 4° in vacuo. | 100 parts by weight con- tains per cent. H ₂ SO ₄ . |
|-----------------------------------|--|-----------------------------------|--|
| 1.000 | 0.09 | 1.650 | 72.82 |
| 1.050 | 7.37 | 1.700 | 77.17 |
| 1.100 | 14.35 | 1.750 | 81.56 |
| 1.150 | 20.91 | 1.800 | 86.90 |
| 1.200 | 27.32 | 1.810 | 88.30 |
| 1.250 | 33.43 | 1.820 | 90.05 |
| 1.300 | 39.19 | 1.830 | 92.10 |
| 1.350 | 44.82 | 1.834 | 93.05 |
| 1.400 | 50.11 | 1.840 | 95.60 |
| 1.450 | 55.03 | 1.8415 | 97.70 |
| 1.500 | 59.70 | 1.840 | 99.20 |
| 1.550 | 64.26 | 1.8385 | 99.95 |
| 1.600 | 68.51 | 1.8384 | 100.00 |

TABLE XI.—Table of Specific Gravity and Percentage Composition of Solutions of Nitric Acid at 15°. Water at 4° = 1.

(Lunge and Rey.)

| Sp. gr. 15° 4° in vacuo. | 100 parts by weight con- tain per cent. HNO ₃ . | Sp. gr. 15° 4° in vacuo. | 100 parts by weight con- tain per cent. HNO ₃ . |
|-----------------------------------|---|-----------------------------------|---|
| 1.000 | 0.10 | 1.400 | 63.30 |
| 1.050 | 8.99 | 1.415 | 68.63 |
| 1.100 | 17.11 | 1.450 | 77.28 |
| 1.150 | 24.84 | 1.500 | 94.09 |
| 1.200 | 32.36 | 1.505 | 96.39 |
| 1.250 | 39.82 | 1.510 | 98.10 |
| 1.300 | 47.49 | 1.515 | 99.07 |
| 1.350 | 55.79 | 1.520 | 99.67 |

TABLE XII.—Table of Specific Gravity and Percentage Composition of Solutions of Alcohol and Water at Various Temperatures. Water at 4° = 1.

(Mendelejeff.)

| Per cent. by weight of alcohol. | Specific gravity of alcohol-water mixtures. | | | |
|---------------------------------------|---|---------|---------|---------|
| | At 0°. | At 10°. | At 20°. | At 30°. |
| 0 | 0.99988 | 0.99975 | 0.99831 | 0.99579 |
| 5 | 0.99135 | 0.99113 | 0.98945 | 0.98680 |
| 10 | 0.98493 | 0.98409 | 0.98195 | 0.97892 |
| 15 | 0.97995 | 0.97816 | 0.97527 | 0.97142 |
| 20 | 0.97566 | 0.97263 | 0.96877 | 0.96413 |
| 25 | 0.97115 | 0.96672 | 0.96185 | 0.95628 |
| 30 | 0.96540 | 0.95998 | 0.95403 | 0.94751 |
| 35 | 0.95784 | 0.95174 | 0.94514 | 0.93813 |
| 40 | 0.94939 | 0.94255 | 0.93511 | 0.92787 |
| 45 | 0.93977 | 0.93254 | 0.92493 | 0.91710 |
| 50 | 0.92940 | 0.92182 | 0.91400 | 0.90577 |
| 55 | 0.91848 | 0.91074 | 0.90275 | 0.89456 |
| 60 | 0.90742 | 0.89944 | 0.89129 | 0.88304 |
| 65 | 0.89595 | 0.88790 | 0.87961 | 0.87125 |
| 70 | 0.88420 | 0.87613 | 0.86781 | 0.85925 |
| 75 | 0.87245 | 0.86427 | 0.85580 | 0.84719 |
| 80 | 0.86035 | 0.85215 | 0.84366 | 0.83483 |
| 85 | 0.84789 | 0.83967 | 0.83115 | 0.82232 |
| 90 | 0.83482 | 0.82665 | 0.81801 | 0.80918 |
| 95 | 0.82119 | 0.81291 | 0.80433 | 0.79553 |
| 100 | 0.80625 | 0.79788 | 0.78945 | 0.78096 |

TABLE XIII. — Table of the Solubility of Sodium Chloride in Water.

100 PARTS OF WATER BY WEIGHT DISSOLVE THE GIVEN WEIGHTS.
(*De Coppet.*)

| Temp. Deg. | NaCl. g. | Temp. Deg. | NaCl. g. | Temp. Deg. | NaCl. g. |
|---------------|-------------|---------------|-------------|---------------|-------------|
| —14 | 32.5 | 15.6 | 35.76 | 59.75 | 37.31 |
| — 6.25 | 34.22 | 20.85 | 35.63 | 71.3 | 37.96 |
| — 5.95 | 34.17 | 25.45 | 35.90 | 74.45 | 37.96 |
| 0 | 35.6 | 38.55 | 36.52 | 82.05 | 38.41 |
| 3.6 | 35.79 | 44.75 | 36.64 | 86.7 | 38.47 |
| 5.3 | 35.94 | 52.5 | 37.04 | 93.65 | 38.90 |
| 14.45 | 35.94 | 55 | 36.99 | 101.7 | 40.76 |

APPENDIX D. DISSOCIATION CONSTANTS OF ORGANIC ACIDS AND BASES.

Ostwald's Dilution Formula. When an electrically neutral molecule, A , dissociates,

$$A = n_1A_1 + n_2A_2 + \dots \quad (1)$$

it follows in accordance with the law of mass action that

$$Kc = c_1^{n_1} \cdot c_2^{n_2} \dots \quad (2)$$

The same formula applies to the dissociation of electrolytes, if c be chosen to represent the concentration of the undissociated part in terms of gram molecules per liter, and c_1 and c_2 the concentrations of the ions (dissociation products) in terms of gram ions per liter. Since the ions occur in electrically equivalent amounts, the following formula holds for a binary electrolyte:

$$Kc = c_1^2 \quad (3)$$

And if a represents the degree of dissociation (part dissociated) determined by any of the various physical methods — e.g. osmotic pressure methods or the electrical conductivity method, — and if V represents the volume which contains one gram molecular weight, then it follows that

$$c = \frac{(1 - a)}{V} \quad \text{and} \quad c_1 = \frac{a}{V}; \quad (4)$$

consequently, from equations (3) and (4),

$$KV(1 - a) = a^2, \quad (5)$$

$$\text{or} \quad K = \frac{a^2}{(1 - a)V}. \quad (6)$$

In other words, the undissociated part per unit volume is proportional to the product of the concentrations of the constituent

ions, and the proportionality factor is called the **Dissociation Constant** or **Ionization Constant**. This formula, known as Ostwald's dilution formula, applies rigorously only to the less active acids and bases.

Furthermore, solving this equation for a ,

$$a = \frac{KV}{2} \left(\sqrt{1 + \frac{4}{KV}} - 1 \right). \quad (8)$$

Most of the constants given in the following tables are numerically equal to 100 times the constants obtained by Ostwald's dilution formula. Such values are designated by the symbol 100 K . In a few cases, other multiples are used. In the system of notation employed to designate these values, 10^{10} stands for unity followed by ten ciphers; 10^{-10} means a decimal point followed by nine ciphers and unity.

$$10^{10} = \frac{1}{10^{-10}} = 10,000,000,000$$

$$10^{-10} = \frac{1}{10^{10}} = 0.0000000001.$$

TABLE XIV. — A Comparison of the Dissociation Constants of Certain Weak Acids, Organic and Inorganic. Temperature = 25°.

| Substance. | Formula. | $K \times 10^{10}$. |
|---|------------------------------------|----------------------|
| Nitrous (Bauer)..... | H.NO_2 | 6,400,000 |
| Acetic..... | $\text{H.C}_2\text{H}_3\text{O}_2$ | 180,000 |
| Carbonic..... | $\text{H.CO}_3\text{H}$ | 3,040 |
| Hydrogen sulphide..... | H.SH | 570 |
| Boric..... | $\text{H.BO}_3\text{H}_2$ | 17 |
| Prussic..... | H.NC | 13 |
| Phenol..... | $\text{H.OC}_6\text{H}_5$ | 1.3 |
| Water($\text{C}_\text{H}^+ \text{C}_\text{OH}^- = \text{K}_{\text{H}_2\text{O}}$) | H.OH | 0.00011 + |

TABLE XV. — Monobasic Fatty Acids and Some of their Substitution Products. Temperature = 25°.

| Substance. | Formula. | 100 K. |
|---|---|---------|
| Formic (Ostwald). | H.CO ₂ H | 0.02140 |
| Acetic (Ostwald) .. | CH ₃ .CO ₂ H | 0.00180 |
| Propionic..... | CH ₃ .CH ₂ .CO ₂ H | 0.00145 |
| Butyric..... | CH ₃ .(CH ₂) ₂ .CO ₂ H | 0.00175 |
| Valerianic..... | CH ₃ .(CH ₂) ₃ .CO ₂ H | 0.00156 |
| Caproic..... | CH ₃ .(CH ₂) ₄ .CO ₂ H | 0.00147 |
| Heptylic..... | CH ₃ .(CH ₂) ₅ .CO ₂ H | 0.00146 |
| HALOGEN DERIVATIVES OF ACETIC ACID. (OSTWALD.) | | |
| Monochloracetic... | CH ₂ Cl.CO ₂ H | 0.155 |
| Dichloracetic..... | CHCl ₂ .CO ₂ H | 5.144 |
| Trichloracetic..... | CCl ₃ .CO ₂ H | 120.00 |
| A SERIES OF SUBSTITUTION PRODUCTS OF ACETIC ACID ILLUSTRATING THE EFFECT OF VARIOUS UNIVALENT SUBSTITUENTS UPON THE DISSOCIATION CONSTANT. (OSTWALD.) | | |
| Acetic..... | CH ₃ .CO ₂ H | 0.0018 |
| Phenylacetic..... | CH ₂ (C ₆ H ₅).CO ₂ H | 0.00556 |
| Glycollic..... | CH ₂ (OH).CO ₂ H | 0.0152 |
| Thioglycollic..... | CH ₂ (SH).CO ₂ H | 0.0225 |
| Monobromacetic.. | CH ₂ Br.CO ₂ H | 0.138 |
| Monochloracetic .. | CH ₂ Cl.CO ₂ H | 0.155 |
| Malonic..... | CH ₂ (CO ₂ H).CO ₂ H | 0.163 |
| Sulphocyanacetic.. | CH ₂ (SCN).CO ₂ H | 0.265 |
| Cyanacetic..... | CH ₂ (CN).CO ₂ H | 0.370 |
| DERIVATIVES OF PROPIONIC ACID SHOWING THE INFLUENCE OF VARIOUS SUBSTITUENTS UPON THE DISSOCIATION CONSTANT. | | |
| Propionic..... | CH ₃ .CH ₂ .CO ₂ H | 0.00145 |
| β-Hydroxypropionic | CH ₂ (OH).CH ₂ .CO ₂ H | 0.00311 |
| Lactic..... | CH ₃ .CH(OH).CO ₂ H | 0.0138 |
| Glyceric..... | CH ₂ (OH).CH ₂ (OH).CO ₂ H | 0.0228 |
| Iodopropionic..... | CH ₂ ICH ₂ .CO ₂ H | 0.0090 |
| Trichlorolactic | CCl ₃ .CH(OH).CO ₂ H | 0.465 |

TABLE XVI. — Dibasic Acids and Some of their Substitution Products. (Ostwald.) Temperature = 25°.

| Substance. | Formula. | 100 K. |
|--|--|-------------|
| Oxalic | COOH.COOH | Large (10?) |
| Malonic (Walden) .. | CH ₂ (COOH) ₂ | 0.163 |
| Succinic | C ₂ H ₄ (COOH) ₂ | 0.00665 |
| Glutaric | C ₃ H ₆ (COOH) ₂ | 0.00475 |
| Adipic | C ₄ H ₈ (COOH) ₂ | 0.0037 |
| Pimelic | C ₅ H ₁₀ (COOH) ₂ | 0.0032 |
| DIBASIC UNSATURATED ACIDS ILLUSTRATING THE RELATION BETWEEN CONFIGURATION AND DISSOCIATION CONSTANTS. | | |
| Maleïc | H—C—COOH | 1.17 |
| Fumaric | H—C—COOH H—C—COOH HOOC—C—H | 0.093 |
| HYDROXY DERIVATIVES OF DIBASIC ACIDS. | | |
| Succinic | C ₂ H ₄ .(COOH) ₂ | 0.00665 |
| i-Malic | C ₂ H ₃ (OH).(COOH) ₂ | 0.0399 |
| Tartaric (d-, l-, r-) | C ₂ H ₂ (OH) ₂ .(COOH) ₂ | 0.097 |

TABLE XVII. — Benzoic Acid and Some of its Substitution Products. (Ostwald.) Temperature = 25°.

| Substance. | Formula. | 100 K. |
|----------------------------------|----------------------|---------|
| Benzoic (Bauer)..... | $C_6H_5.COOH$ | 0.0073 |
| Cinnamic..... | $C_6H_5.CH=CH.COOH$ | 0.00355 |
| o-Nitrobenzoic..... | $C_6H_4.NO_2.COOH$ | 0.616 |
| p-Nitrobenzoic..... | $C_6H_4.NO_2.COOH$ | 0.0396 |
| m-Nitrobenzoic..... | $C_6H_4.NO_2.COOH$ | 0.0345 |
| m-Chlorbenzoic..... | $C_6H_4.Cl.COOH$ | 0.0155 |
| o-Chlorbenzoic..... | $C_6H_4.Cl.COOH$ | 0.0132 |
| p-Chlorbenzoic..... | $C_6H_4.Cl.COOH$ | 0.0093 |
| o-Hydroxybenzoic, salicylic..... | $C_6H_4.(OH).COOH$ | 0.102 |
| m-Hydroxybenzoic..... | $C_6H_4.(OH).COOH$ | 0.0087 |
| p-Hydroxybenzoic..... | $C_6H_4.(OH).COOH$ | 0.0029 |
| Dihydroxybenzoic (2, 6).... | $C_6H_3.(OH)_2.COOH$ | 5.00 |
| Dihydroxybenzoic (2, 3).... | $C_6H_3.(OH)_2.COOH$ | 0.114 |
| Dihydroxybenzoic (2, 5).... | $C_6H_3.(OH)_2.COOH$ | 0.108 |
| Dihydroxybenzoic (2, 4).... | $C_6H_3.(OH)_2.COOH$ | 0.052 |

TABLE XVIII. — Phenol and Some of its Substitution Products. Temperature = 25°.

| Substance. | Formula. | 100 K. |
|------------------------------------|----------------------|-------------|
| Phenol (Walker)..... | $C_6H_5.OH$ | 0.000000013 |
| o-Nitrophenol (Bader)..... | $C_6H_4.NO_2.OH$ | 0.000043 |
| m-Nitrophenol (Bader)..... | $C_6H_4.NO_2.OH$ | 0.000012 |
| p-Nitrophenol (Bader)..... | $C_6H_4.NO_2.OH$ | 0.0000089 |
| Dinitrophenol (1, 2, 6) (Bader)... | $C_6H_3.(NO_2)_2.OH$ | 0.0174 |
| Dinitrophenol (1, 2, 4) (Bader)... | $C_6H_3.(NO_2)_2.OH$ | 0.008 |
| Dinitrophenol (1, 3, 6) (Bader)... | $C_6H_3.(NO_2)_2.OH$ | 0.0007 |
| Dinitrophenol (1, 2, 3) (Bader)... | $C_6H_3.(NO_2)_2.OH$ | 0.0012 |
| Dinitrophenol (1, 3, 4) (Bader)... | $C_6H_3.(NO_2)_2.OH$ | 0.0004 |

TABLE XIX. — Dissociation Constants of Some Organic Bases. (Bredig.) Temperature = 25°.

| Substance. | Formula of the Base. | 100 K. |
|----------------------------|--|---------------------------|
| ALIPHATIC AMINES. | | |
| Ammonia..... | $\text{HNH}_3.\text{OH}$ | 0.0023 |
| Methylamine..... | $\text{CH}_3\text{NH}_3.\text{OH}$ | 0.050 |
| Ethylamine..... | $\text{C}_2\text{H}_5\text{NH}_3.\text{OH}$ | 0.056 |
| Dimethylamine..... | $(\text{CH}_3)_2\text{NH}_2.\text{OH}$ | 0.074 |
| Diethylamine..... | $(\text{C}_2\text{H}_5)_2\text{NH}_2.\text{OH}$ | 0.126 |
| Trimethylamine..... | $(\text{CH}_3)_3\text{NH}.\text{OH}$ | 0.0074 |
| Triethylamine..... | $(\text{C}_2\text{H}_5)_3\text{NH}.\text{OH}$ | 0.064 |
| Urea..... | $\text{CO}(\text{NH}_2)_2\text{H}.\text{OH}$ | $K = 1.6 \times 10^{-14}$ |
| AROMATIC AMINES. | | |
| Aniline..... | $\text{C}_6\text{H}_5\text{NH}_3.\text{OH}$ | $K = 1.1 \times 10^{-10}$ |
| Benzylamine..... | $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3.\text{OH}$ | 2.4×10^{-5} |
| o-Nitraniline (Farmer).... | $\text{C}_6\text{H}_4\text{NO}_2\text{NH}_3.\text{OH}$ | 6×10^{-14} |
| m-Nitraniline..... | $\text{C}_6\text{H}_4\text{NO}_2\text{NH}_3.\text{OH}$ | 4×10^{-12} |
| p-Nitraniline..... | $\text{C}_6\text{H}_4\text{NO}_2\text{NH}_3.\text{OH}$ | 1.2×10^{-13} |

REFERENCE TO THE LITERATURE.

- Ostwald, *Z. für Phys. Chem.*, **3**, 170; **31**, 433. Bredig, *Z. für Phys. Chem.*, **13**, 289.
Walker, *Z. für Phys. Chem.*, **4**, 319. Walker, *Z. für Phys. Chem.*, **32**, 137.
Bader, *Z. für Phys. Chem.*, **6**, 289. Bauer, *Z. für Phys. Chem.*, **56**, 218.
Walden, *Z. für Phys. Chem.*, **8**, 433.

APPENDIX E. HYDROLYSIS OF SALTS OF WEAK ACIDS AND WEAK BASES.

TABLE XX.

Temperature = 25°.

(From Walker's Physical Chemistry.)

| Substance. | Formula. | Per cent. of hydrolysis. |
|---|--|--------------------------|
| <i>Salts of Weak Acids</i> $\frac{N}{10}$ | | |
| Potassium phenolate..... | KOC ₆ H ₅ | 3.1 |
| Potassium cyanide..... | KNC | 1.1 |
| Sodium tetraborate..... | Na ₂ B ₄ O ₇ | 0.5 |
| Sodium acetate..... | NaC ₂ H ₃ O ₂ | 0.01 |
| <i>Salts of Weak Bases</i> $\frac{N}{10}$ | | |
| Aniline hydrochloride..... | C ₆ H ₅ NH ₃ .Cl | 1.4 |
| p-Toluidine..... | CH ₃ C ₆ H ₄ NH ₃ .Cl | 0.9 |
| o-Toluidine..... | CH ₃ C ₆ H ₄ NH ₃ .Cl | 1.8 |
| Urea hydrochloride..... | NH ₂ CONH ₃ .Cl | 89.3 |
| <i>Concentration</i> $\frac{N}{32}$ | | |
| o-Nitraniline hydrochloride .. | NO ₂ C ₆ H ₄ NH ₃ .Cl | 98.6 |
| m-Nitraniline hydrochloride .. | NO ₂ C ₅ H ₄ NH ₃ .Cl | 26.6 |
| p-Nitraniline hydrochloride .. | NO ₂ C ₅ H ₄ NH ₃ .Cl | 79.6 |
| Acetanilide hydrochloride.... | C ₆ H ₅ .N(COCH ₃)H ₂ .Cl | 99.8 |

APPENDIX F. LIST OF APPARATUS NEEDED
TO PERFORM THE EXPERIMENTS IN
THIS OUTLINE.
(ORIGINAL OUTFIT.)

RETURNABLE ARTICLES.

- 1 Adapter, bent.
- 2 Bottles, vial-mouthed, 1000 c.c., plain.
- 4 " wide- " 250 c.c., "
- 2 " vial- " 250 c.c., "
- 1 Bucket, small, granite ware.
- 2 Bunsen burners.
- 1 Calcium chloride tube, straight, 18 cm.
- 1 " " " " 25 cm.
- 2 Clamps and attachments.
- 1 Condenser, Liebig's, 55 cm.
- 1 Cork borer, set of 5 and handle.
- 1 Crucible, iron, 6 cm.
- 1 Crucible tongs, iron.
- 1 Cylinder, grad., 100 c.c.
- 1 Desiccator, Scheibler's, 10 cm. with side tube.
- 1 Dropping-tube, cf. § 16.
- 1 Evaporating dish, 7 cm.
- 1 " " " 10 cm.
- 1 " " " 12 cm.
- 1 Filter pump and attachment.
- 2 Flasks, flat bottom, 30 c.c.
- 4 Flasks, flat bottom, 100 c.c.
- 2 " " " 300 c.c.
- 2 " " " 500 c.c.
- 1 Flask, " " 1000 c.c.
- 1 " round bottom, 500 c.c.
- 1 " filtering, 250 c.c.
- 1 " distilling, 15 c.c.
- 1 " " 30 c.c.
- 1 " " 50 c.c.
- 1 " " 150 c.c.
- 1 Fractionating-column, cf. § 1.

RETURNABLE ARTICLES.

- 2 Funnels, 65 mm.
- 1 Funnel, 10 mm.
- 1 " Büchner, $6\frac{1}{2}$ cm.
- 1 " dropping, 60 c.c.
- 1 " separatory, 250 c.c.
- 4 Glass plates, 4×4 inches.
- 1 Mortar and pestle.
- 1 Nest of beakers, 50 c.c. to 600 c.c.
- 1 Pinch clamp, Mohr's.
- 3 Rings, iron, three sizes.
- 1 Sand bath, sheet iron.
- 1 Screw clamp.
- 1 Spatula, porcelain, 10 cm.
- 1 Stand, iron, small.
- 1 Stand, iron, medium.
- 24 Test-tubes, 160×15 mm.
- 1 Test-tube holder.
- 1 Thermometer, 360° .
- 1 Thistle tube.
- 1 Tripod, iron.
- 1 Tube, hard glass combustion, 25 cm., cf. § 20.
- 1 Watch glass, 50 mm.
- 1 " " 75 mm.
- 1 " " 100 mm.
- 1 Water bath.
- 1 Set of weights, 10 mg. to 50 g.

NON-RETURNABLE ARTICLES.

- 1 Clay triangle.
- 1 File, triangular.
- 1 File, round.
- 5 ft. Glass rod, 4 mm.
- 5 ft. Glass tubing, 6 mm.
- 1 Package of filter paper, 9 cm.
- 1 ft. Pure gum rubber tubing, $\frac{1}{8}$ in.
- 9 ft. Rubber gas tubing.
- 1 Sponge.
- 1 Test-tube brush.
- 1 Towel.
- 1 Wire gauze.

LIST OF SPECIAL APPARATUS USED ONLY IN ONE EXPERIMENT.

Asbestos paper, thin, § 18.

Bath, Wood's metal, § 57.

" oil, § 57.

Fractionating-column, special form, § 23.

Galvanometer, § 22.

Kipp's apparatus, § 173.

Manometer, § 120.

Pipette, 5 c.c. grad. in 0.1 c.c., § 96.

Platinum electrodes, § 22.

" wire, fine, § 18.

Sodium press, § 17.

Soxhlet extractor, § 102.

Two-liter flask, § 57.

APPENDIX G. SOME SPECIAL APPARATUS FOR PREPARING REAGENTS.

GASES.

a. **Kipp's Apparatus.** Many gases (CO_2 , H_2S , H , etc.) which can be prepared by the action of liquid reagents upon solids, may be made in small amounts for laboratory uses by means of a **Kipp Generator**. The solid in large pieces rests upon the

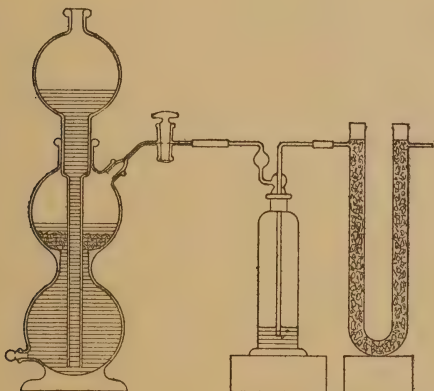


Fig. 24. Kipp's Apparatus.

shoulders of the middle glass compartment. The liquid reagent, usually water or acid, is poured into the upper glass globe, from which it flows to the bottom compartment, and thence to the solid. The upper chamber serves as a reservoir to accommodate the liquid which, by the pressure of gas evolved after the flow of gas has been stopped, is forced away from the central and lower compartment. The gas generated passes through the stop-cock to appropriate apparatus containing reagents for

washing it or drying it. For this purpose, it is convenient to use a **Drechsel Wash-bottle** charged either with wash liquid or with drying agents. Large **U-tubes** charged with drying or

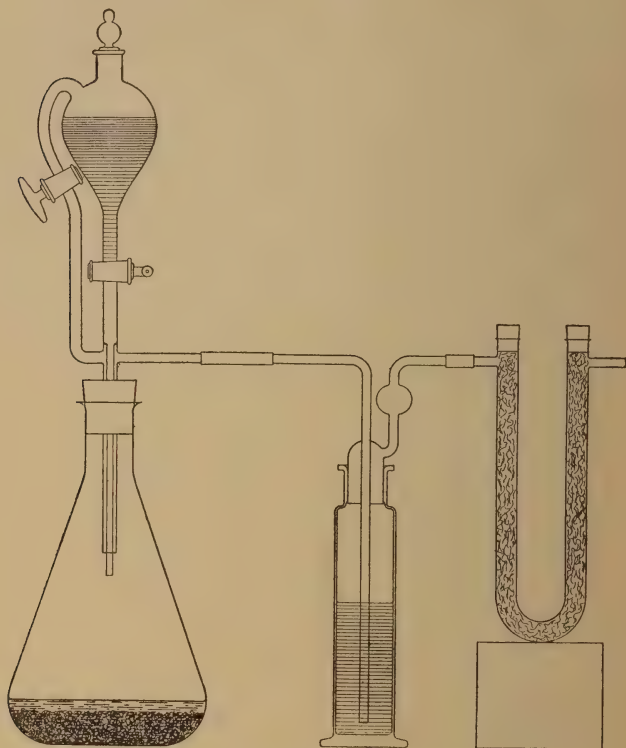


Fig. 25. Dropping-generator.

purifying agents are frequently desirable; e.g., calcium chloride or phosphorus pentoxide to remove water vapor, soda-lime to remove acid vapor, lead acetate on glass beads to remove hydrogen sulphide.

When considerable quantities of such gases are required, it is

now customary to prepare them in large, specially constructed generators, or to supply them from **cylinders of compressed gas** (oxygen, hydrogen, carbon dioxide, etc.) connected with pipe systems. By means of a pressure reducing device at some central supply station, the pressure at which gases from such cylinders are delivered can be regulated and set as required.

b. The Dropping-generator. A very convenient form of gas generator, known as the dropping-generator, devised by Mr. Freas* of the University of Chicago, has proved very useful in preparing many gases in which liquids must be added during the process, and must be admitted to the generator flask while the gas, under some pressure, is being evolved.

The following table will illustrate some of the reactions which may be carried out with the dropping-generator.

TABLE XXI.

| Reagent used in the Dropping-generator. | Reagent used in the Flask. | Gas Produced. |
|--|--|------------------------|
| HCl (dil.) | NaHCO_3 | CO_2 |
| H_2O | Na_2O_2 (oxone) | O_2 |
| HCl (dil.) | FeS (powd.) | H_2S |
| HCl (dil.) | Zn (dust) | H_2 |
| NaNO_2 (sat. sol.) | HCl (dil.) + FeCl_2 (heat) | NO |
| NaNO_2 (sat. sol.) | NH_4Cl + H_2O (heat) | N_2 |
| HCl (dil.) | NaHSO_3 | SO_2 |
| HCl (conc.) | KMnO_4 | Cl_2 |
| H_2SO_4 (conc.) | NH_4Cl | HCl |
| H_2O | CaC_2 | C_2H_2 |
| $\text{C}_2\text{H}_5\text{OH}$ (abs. alcohol) | H_3PO_4 (sp. gr. 1.73) (heat) | C_2H_4 |
| Br_2 | P (red) + H_2O | HBr |

A dropping-funnel of the usual kind is modified by providing it with a side tube of glass which connects the space above the liquid in the funnel with the interior of the generator flask, thus equalizing the pressure at the two places while the liquid, regulated by a stop-cock, is allowed to flow into the flask. A second stop-cock sealed in the pressure equalizing tube must be closed when it becomes necessary during the operation to pour more

* Thomas B. Freas, School Science and Mathematics, February, 1907.

liquid into the funnel. The gas passes from the flask through the annular space between the two tubes at the bottom of the dropping-generator, where an exit tube conducts it to a wash-bottle.

This device greatly facilitates the setting up of apparatus, especially for lecture demonstration, since it does away with the usual cumbersome connections made by means of three-holed stoppers.



Fig. 26. The Dissolving-tube.

cover the end of the wide tube which leads to the side tube of the dropping-tube. A notch cut in the cork of the bottle permits air to enter.

When the materials are ready, the dissolving-tube is closed with a rubber-stopper which fits it air-tight. By means of a stop-cock inserted in this stopper, air is drawn from the apparatus until the liquid has risen and filled the dissolving-tube to a point slightly above the opening of the side tube. When the stop-cock is closed, the denser liquid around the solid will fall to the bottom

SOLUTIONS.

a. The Dissolving-tube. The problem of making filtered solutions of difficultly soluble crystalline solids — such as mercuric chloride, copper sulphate, potassium dichromate, silver nitrate, etc. — is one which causes considerable inconvenience when time is an item. A simple device suggested by Mr. Freas* of the University of Chicago is very useful for such purposes. It permits of the making of filtered solutions of any desired strength up to saturated solutions.

The weighed solid is placed on a filter-plug of cotton or of glass-wool in the chamber of the dissolving-tube. An ordinary 2-liter acid bottle contains the measured solvent, which should fill the bottle to a point sufficiently high to permit enough water or liquid to be drawn up to fill the dissolving-tube; at the same time sufficient water should be left in the bottle to

* Thomas B. Freas, *School Science and Mathematics*, February, 1907.

of the bottle through the longer tube, and will thus displace pure solvent at the surface of the liquid in the bottle. A continuous flow of the liquid will begin, and will not cease until all of the solid has disappeared or the solution has become saturated.

b. The Soxhlet Extractor (see page 91, Fig. 21) will be found very serviceable when it is desirable to make a separation of two or more substances by means of a limited amount of solvent. The mixture to be extracted is placed in an extraction thimble* indicated in the illustration by dotted lines. The solvent is poured into the flask and heated until it boils. The vapors pass from the flask through the wide tube to the left in the illustration, and are condensed in the Liebig's condenser at the top. The liquid then drops upon the mixture in the thimble. When the level of the liquid in the main compartment reaches the level of the bend at the top of the small side tube at the left in the illustration, the solvent with some dissolved substance syphons back into the flask. This action continues until the mixture in the thimble is completely extracted.

* Extraction thimbles for this purpose are made by Schleichert and Schüll, and may be purchased through any large dealer in chemical supplies.

APPENDIX H. LISTS OF GASES, LIQUIDS, AND SOLIDS USED AS REAGENTS FOR ORGANIC CHEMISTRY.

The following lists include the reagents needed to perform all of the experiments included in the outline. Whenever a reagent is used more than ten times in the outline, that is in more than ten different sections, no section numbers are given in the lists. In all other cases the numbers of all sections in which each reagent is used are printed in bold type.

The **letters S.R.** after a name indicate that it is not advisable to put that substance on the side-shelves. Such substances are either dangerous or costly. They may be set out for the particular experiment, or better still, in many cases, they may be distributed to students at the storeroom.

The **concentrations** of the solutions are given in most instances. In order that the student may be informed of the approximate strength of each solution he uses, the solutions have been made of some definite normality, usually normal (N.), molar, half-normal ($\frac{1}{2}$ N.), or tenth-normal ($\frac{1}{10}$ N.). In a few special cases, the concentrations are expressed in terms of per cent. The number in parentheses following the symbol designating concentration is the weight or volume of a substance required with water to make one liter of the solution. Sat. = saturated. In the case of hydrates, the calculations are based upon the use of the commonest commercial hydrate. Unless this is the case, the formula of the substance used will be given.

It is desirable to place on the labels of the reagent bottles all of the information given above. This will inform the student, as well as the person who makes the solution, as to the exact nature of the contents of each bottle.

When the experiments to be performed have been decided upon, it will be possible to exclude from the list of reagents for the shelves all materials which are shown in the following lists to be required only for experiments outside of those chosen.

GASES.

| | SECTION. |
|----------------------|--------------------|
| Ammonia..... | 25 |
| Carbon dioxide..... | 130, 137, 163, 173 |
| Chlorine..... | 81 |
| Hydrogen..... | 173 |
| " chloride..... | 94, 137 |
| " sulphide..... | 43 |
| Sulphur dioxide..... | 27, 103 |

LIQUIDS AND SOLUTIONS.

(500 c.c. narrow-mouthed bottles.)

| | |
|---|---|
| Acetic acid, glacial..... | 32, 38, 94, 108, 115, 117, 165, 166, 167 |
| " " dilute, 6 N., (420 c.c. of 80 per cent.). | |
| " anhydride..... | 86, 141, 143 |
| " ethyl ester..... | 45 |
| Acetone..... | 14, 15, 28, 29, 31, 32, 50, 57, 93, 170 |
| Acetoacetic ethyl ester..... | 87, 168 |
| Acetylacetone..... | 63 |
| Acetyl chloride..... | 41, 108 |
| Alcohol, 95 per cent. | |
| Aluminium chloride, $\frac{1}{10}$ molar, ($\frac{3}{10}$ N.)..... | 96, 105 |
| " sulphate, N., (111)..... | 51, 161 |
| Ammonium chloride, 4N., (213.5)..... | 7, 51, 161 |
| " ferric sulphate, 10 per cent..... | 65 |
| " hydroxide, 6 N., (400 c.c.)..... | 7, 45, 74, 78 |
| " " com'l., 7 N. | |
| Amylene..... | 6 |
| Amyl alcohol..... | 11 |
| Amyl nitrite..... | 109 |
| Aniline..... | 105, 108, 112, 115, 120, 125, 141, 154, 172 |
| Aniline solution, sat., $\frac{1}{3}$ N..... | 57 |
| l-Arabinose..... | 89 |
| Barium chloride, $\frac{1}{10}$ molar, ($\frac{1}{3}$ N.), (24.4)..... | 96 |
| Benzaldehyde..... | 29, 30, 134, 135, 141, 145, 150, 152 |
| Benzene, benzol..... | 97, 98, 99, 100, 138, 178 |
| Benzoyl chloride..... | 11, 60, 61, 129, 138, 143 |
| Brom benzene, cf. phenyl bromide. | |

| | SECTION. |
|---|-----------------------------------|
| Bromine, element | 51, 66, 157, 165 |
| Bromine solution, 5 per cent. in carbon tetrachloride .. | 6, 97, 127 |
| Bromine water, sat., $\frac{1}{3}$ N., (15 c.c.) | 5, 7, 50, 88, 78, 127 |
| Butyl alcohol, iso | 14 |
| Calcium chloride, $\frac{1}{10}$ molar, ($\frac{1}{3}$ N.), (21.9 cryst.) .. | 64, 65, 95, 96 |
| " hydroxide, lime-water, sat., $\frac{1}{25}$ N. (2 as CaO). | |
| Carbon disulphide | 74, 76, 138, 162 |
| Chloroform | 4, 8, 45, 52, 58, 63 |
| Chromic acetate | 161 |
| Cupric sulphate, N., (125) | 4, 51, 61, 79, 87 |
| Diethylamine, S.R. | 53 |
| Dimethylaniline | 108, 113, 117, 121, 149, 152 |
| Dimethyl sulphate, S.R. | 75, 128 |
| Ethylammonium bromide, $\frac{1}{20}$ N., (6.3) | 8 |
| Ethyl bromide | 8, 53, 55 |
| Ethyl ether, absolute | 137, 174 |
| Ethyl iodide, S.R. | 173 |
| Ethyl malonic acid, S.R. | 67 |
| Ferric chloride, N., (90). | |
| Ferric hydroxide, colloidal sol. | 95 |
| Ferrous sulphate, $\frac{1}{10}$ N. | 44, 83 |
| Fehling's solution | 26, 30, 89, 90, 91, 104, 120, 150 |
| Formaldehyde, formaline, 40 per cent. | 22, 94, 149 |
| Glycerol, glycerine | 13, 34, 61, 96, 172 |
| Hydrochloric acid, C.P., conc., 13 N. | |
| " " " dil., 6 N., (467 c.c.) | |
| " " " " $\frac{1}{10}$ N. | 96 |
| Hydrochlorplatinic acid, S.R., 10 per cent. | 52, 53, 105, 172 |
| Hydrogen peroxide, 10 vol. | 50 |
| Hydroxylamine hydrochloride, 10 per cent. | 50 |
| β -Hydroxybutyric acid, S.R. | 83 |
| Iodine solution (1 I : 5 KI: 15 H ₂ O) | 14, 45, 92 |
| Isopropyl alcohol, S.R. | 30, 141 |
| Isopropyl iodide, S.R. | 49 |

| | SECTION. |
|---|-------------------------|
| Lactic acid | 82 |
| Lead acetate, N. | 158, 161 |
| Ligroïne, boiling-point 40°-60° | 6, 31, 98 |
| Litmus, neutral. | |
| Magnesium sulphate, sat. | 96 |
| Mercuric chloride, sat., $\frac{1}{2}$ N., (68) | 34, 48, 82 |
| Methyl alcohol. . . 11, 12, 18, 19, 20, 22, 34, 35, 37, 43, 101, 102, 164 | |
| " iodide, S.R. | 15, 43, 164, 171 |
| " orange, solution | 51 |
| " salicylate | 145 |
| Monomethyl aniline | 108 |
| α -Naphthol, 10 per cent. in chloroform. | 88 |
| Nickel nitrate, N., (145) | 62 |
| Nitric acid, conc., C.P., 16 N. | 99, 100, 130, 131, 151 |
| Nitric acid, dil., 6 N., (382 c.c.) | |
| Nitrobenzene | 101, 102, 105, 172 |
| Nitroethane, S.R. | 48 |
| Petroleum ether, cf. ligroïne. | |
| Phenolphthaleïn sol., (1 g. + 500 c.c. alcohol) | 36 |
| Phenyl bromide, brombenzene | 8, 174 |
| Phenylhydrazine | 32, 93, 139, 140, 168 |
| Phloroglucinol, 1 per cent. sol. | 20 |
| Phosphoric acid, sp. gr., 1.73, 46 N. | 56, 61 |
| Phosphorus trioxide, S.R. | 40 |
| Platinic chloride, cf. hydrochlorplatinic acid. | |
| Potassium bromide, $\frac{1}{2}$ N., (59.5) | 8, 97 |
| " dichromate, $\frac{1}{2}$ N., (74) | 91, 158, 171 |
| " ferrocyanide, 10 per cent. | 65 |
| " hydrogen sulphide, 33 per cent. | 42 |
| " iodide, $\frac{1}{2}$ N., (83) | 22 |
| " nitrate, $\frac{1}{2}$ N., (50.5) | 22 |
| " permanganate, $\frac{1}{2}$ N., (79) | 5, 66, 68, 97, 121, 141 |
| " thiocyanate, 10 per cent. (about $\frac{1}{10}$ N.) | 65 |
| Pyridine | 50, 171 |
| Resorcinol, resorcin, 0.5 per cent. sol. | 19 |

| | SECTION. |
|--|--------------------|
| Schiff's reagent..... | 29, 30 |
| Silver nitrate, $\frac{1}{4}$ N., (42.5) . . . 8, 9, 22, 23, 34, 36, 43, 81, 82, 84, 134 | |
| Soap solution, neutral..... | 36 |
| Sodium acetate, N., (136 cryst.) | |
| " bromide, $\frac{1}{10}$ molar, ($\frac{1}{10}$ N.), (10.3) | 95 |
| " carbonate, N., (53 anhydrous) | 5, 121, 127, 134 |
| " chloride, $\frac{1}{10}$ molar, ($\frac{1}{10}$ N.), (5.85)..... | 95 |
| " " sat., 5.5 N., (322) | 16, 57, 98 |
| " hydrogen phosphate (Na_2HPO_4) molar | 95 |
| " hydrogen sulphite, (bisulphite, 40 per cent.) .28, 134, 146 | |
| " hydroxide, $\frac{1}{10}$ N., (4.0) | 96 |
| " iodide, $\frac{1}{10}$ molar, ($\frac{1}{10}$ N.)..... | 95 |
| " sulphate, $\frac{1}{10}$ molar, $\frac{1}{5}$ N., (32.2)..... | 95 |
| Sulphuric acid, conc., C.P., 36 N.,..... | 126, 127, 131, 135 |
| " " dil., C.P., 6 N., (167 c.c.). | |
| Tollen's reagent..... | 26, 30 |
| Toluene | 98, 167 |
| Turkey-red oil | 161 |
| I-Xylose 5 per cent. sol. | 89 |
| Zinc chloride, $\frac{1}{2}$ N., (68 cryst.)..... | 105 |

SOLIDS.

(250 c.c. wide-mouthed bottles.)

| | |
|--|----------|
| Acetamide | 46, 51 |
| Acetanilid | 44 |
| Albumin | 96 |
| Alizarin-paste | 164 |
| Aluminium chloride, anhydrous, S.R. | 138 |
| 1,8-Amino-naphthol, 3,6-disulphonic acid, (H acid) | 118 |
| Ammonium chloride..... | 94 |
| " oxalate | 66 |
| " sulphate | 77 |
| Aniline hydrochloride | 109, 112 |
| Anthracene | 166, 167 |
| Antimonious oxide | 85 |
| Arsenious oxide, powd..... | 36 |

SECTION.

| | |
|--|-------------------|
| Benzidine | 118 |
| Benzoic acid | 3, 153 |
| Bleaching-powder, $\frac{1}{2}$ lb. can, S.R. | 57 |
| Caffeïn, S.R. | 80 |
| Calcium carbide | 7 |
| " chloride, fused sticks. | |
| " chloride, porous fused. | |
| " oxide, quick-lime | 2, 52, 158 |
| Cane-sugar, cf. Sugar. | |
| Casein. | 96 |
| Charcoal, animal | 108, 130 |
| Chloral hydrate | 27 |
| Chromic anhydride (CrO_3) | 30, 167 |
| Cloth, cheese- | 158, 160, 161 |
| " mordanted in strips | 161 |
| Copper turnings | 7, 20, 136 |
| " wire | 8, 19 |
| Congo red | 159 |
| " red paper | 197 |
| Cotton. | |
| Cupric acetate | 63 |
| " chloride | 136 |
| " oxide, powd. | 3, 7, 34, 94, 173 |
| " sulphate, anhydrous. | 2 |
| " " cryst. | 7 |
| Cyanuric acid | 73 |
| Dextrin | 91, 92 |
| Diethyl tartrate | 86 |
| Dimethyl glyoxime | 62 |
| 3,5-Dinitrobenzoic acid | 12 |
| Diphenylamine | 107 |
| Ferric chloride, anhydrous | 23 |
| Ferrous sulphate | 70, 158 |
| Fibrin, blood | 96 |
| Fuchsine | 161 |
| d-Galactose | 89 |
| Gallic acid | 147 |

| | SECTION. |
|---------------------------------------|------------------------------|
| Gelatin..... | 96, 148 |
| Gelatin plates..... | 96 |
| d-Glucose..... | 80, 88 |
| Glutin..... | 96 |
| Glycogen..... | 91, 92 |
| Gum arabic..... | 88, 91, 92 |
| Hydroxylamine hydrochloride, S.R..... | 7, 31, 137, 138 |
| Iodine..... | 9, 14, 57, 58, 92 |
| Indigo, natural..... | 158, 169 |
| Iron filings..... | 97 |
| Lactose, milk-sugar..... | 90 |
| Lead chloride..... | 174 |
| " dioxide..... | 149, 153 |
| Litharge, lead monoxide..... | 34 |
| Litmus paper..... | |
| Magnesium turnings (Grignard)..... | 15, 102, 174 |
| Malachite green..... | 151 |
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APPENDIX I. REAGENT BOTTLES AND RE-AGENT SHELVES.

BOTTLES.

For liquids, 500 c.c. tincture bottles of the type represented in the illustration are very serviceable. The wing stoppers are easily held between the fingers in the usual way while the reagent is being poured. Such stoppers are much to be preferred to

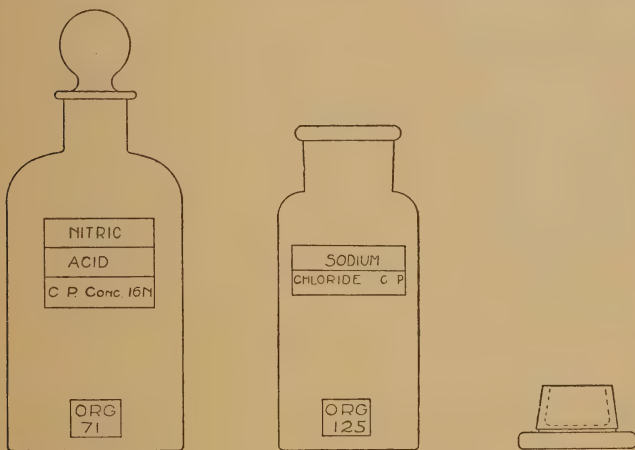


Fig. 27.

flat stoppers for this reason. When flat stoppers are used, they are placed upon the shelf or desk, and in this way are frequently broken or returned to the wrong bottle.

Glass-stoppered salt-mouthed iron-mould bottles, 8 oz. (250 c.c.), with hood tops have been found to be very convenient for solid reagents. The depression in the stopper facilitates the transferring of small amounts to tubes, flasks, etc. It has been

found that this form of reagent bottle induces economy in the use of solids. With the ordinary solid stopper it is customary to pour solids upon slips of paper or upon watch crystals, and to throw away the unused portion.

LABELS.

Narrow gummed labels with cations and anions, or with the common names, such as ethyl, methyl, conc. C.P., etc., printed separately, have been found to be a great convenience in labeling sets of reagents for various laboratories. With comparatively few different kinds of labels countless combinations can be made as required. Sets of such labels can be kept ready for use in small oblong pasteboard boxes arranged alphabetically. Labels may be made to stick firmly to glass by observing the following precautions:—Clean the surface of the glass very carefully with gasoline. Moisten the label thoroughly, and press it firmly against the bottle by means of a piece of blotting paper until all of the air spaces have been removed. If the mounted label, previously warmed, is quickly painted with paraffine heated almost to the boiling-point, and the excess of paraffine is rubbed off, the labels will last for years.

REAGENT SHELVES.

The illustration (Fig. 28) shows a type of reagent shelf which has been used successfully with elementary classes for a number of years. The dimensions of the shelves pictured are 72 in. high \times 39 in. wide \times 5 in. deep. By means of narrow ($\frac{3}{8}$ in.) strips of wood at the sides and back, each bottle is provided with its own numbered compartment. These strips may be fastened so that all bottles, both large and small, shall set 1 inch back from the front of the shelf. If desired, the strips may be beveled in front, and may also be set back 1 inch from the edge of the shelf. This will leave a 1-inch margin in front of the bottles which will make it easy to keep the shelves clean. The bottles have very little free play. As a result of this, they are always opposite the proper number on the shelf, and the reagent shelves as a whole always present an orderly appearance.

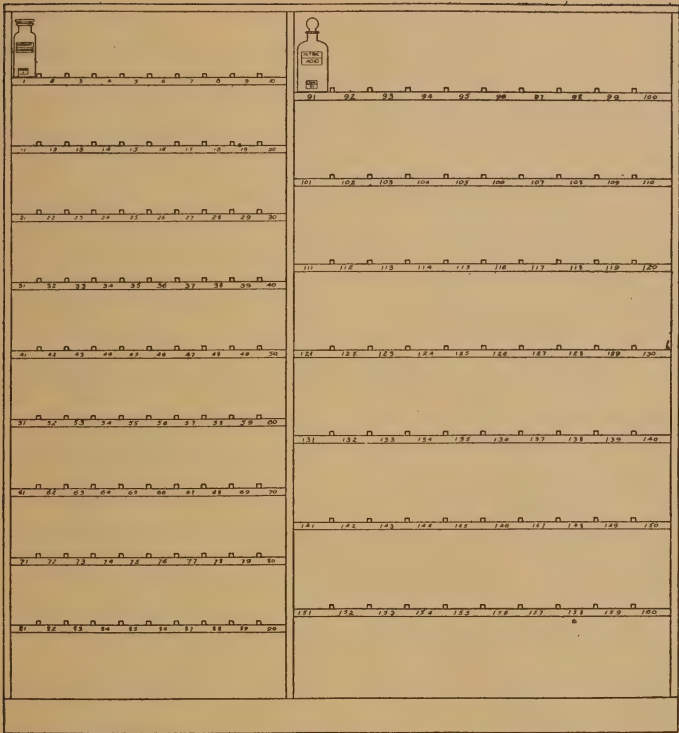


Fig. 28.

Small brass stencils will be found convenient in numbering the compartments. The lower shelves have been made a little wider than the others in order to accommodate a number of small stone-ware jars with covers which have been used for some bulky solids; e.g., copper turnings, marble, nails, sand, etc.

A shelf of the kind illustrated above will accommodate fifty students working at once.

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